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Removing Water-Soluble Hazardous Material Spills from Waterways with Carbon

Rockwell International
Newbury Park, CA

Prepared for

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REMOVING WATER-SOLUBLE HAZARDOUS MATERIAL SPILLS FROM WATERWAYS WITH CARBON

by

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Contract No. 68-03-2648

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Buoyant packets are found to be ineffective for removing spills from waterways. The rapid dilution of spills also renders panels ineffective unless the spill is massive and the response is rapid.

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FOREWORD

The U.S. Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimonies to the deterioration of our natural environment. The complexity of that environment and the interplay of its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution; it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems to prevent, treat, and manage wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, to preserve and treat public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research and provides a most vital communications link between the researcher and the user community.

This report presents an analysis of the use of in-situ activated carbon and other adsorbants for the removal of spilled, water-soluble hazardous substances from waterways. The report will be of interest to all those involved in hazardous materials spill control and countermeasures.

Francis T. Mayo, Director
Municipal Environmental Research
Laboratory

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ABSTRACT

A model for the removal of water-soluble organic materials from water by carbon-filled, buoyant packets and panels is described. Based on this model, equations are derived for the removal of dissolved organic compounds from waterways by buoyant packets that are either (a) cycled through a water column, or (b) suspended in the waterway by natural turbulence, and by panels mechanically suspended in waterways. Computed results are given for phenol spills. The effects of turbulence on the suspension of buoyant packets and of turbulent mixing and longitudinal dispersion of spills in waterways on the removal of water-soluble hazardous materials are considered.

Buoyant packets are found to be ineffective for removing spills from waterways. The rapid dilution of spills also renders panels ineffective unless the spill is massive and the response is rapid.

This report was submitted in partial fulfillment of Contract No. 68-03-2648 by Rockwell International, Environmental Monitoring & Services Center, under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period June 1978 to January 1979, and work was completed as of 15 January 1979.

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ABBREVIATIONS AND SYMBOLS

A_c -- total cross-sectional area of panels normal to the flow direction in the watercourse

A_p -- cross-sectional area of a packet (10.2 cm x 10.2 cm [4 in x 4 in] for this study)

A_t -- cross-sectional area of panels in a section of length x

a -- total exterior particle surface area for mass transfer per unit volume of packed space; defined for spheres in Eq. 6.

a_x -- cross-sectional area of panels in length dx

b -- a reference point in Eq. 30, b = 0.05D

C -- concentration in the bulk fluid

C_b -- concentration at reference point b

C_i -- concentration at exterior of adsorbent particle

C_{in} -- concentration of solute in fluid entering a panel or packet

C_o -- initial concentration

C_{out} -- concentration of solute in fluid exiting a panel or packet

D -- depth of a waterway

D_l -- hydraulic mean depth of a waterway

D_x -- dispersion coefficient in x direction, longitudinal dispersion (cm^2/sec or m^2/sec)

$\mathscr{D}$ -- molecular diffusion coefficient (cm^2/sec)

d -- diameter

d_p -- diameter of particles in packets or panels

E -- rate of energy dissipation per unit mass (ergs/gm-sec)

F_j -- friction factor in Eq. 3 (see Ref. 8)

F_{re} -- a factor used to modify d_p in Reynolds number calculation (see Ref. 8)

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f	--	friction factor for objects moving through fluid
g	--	acceleration due to gravity
h	--	half width of boundaries used in solution of Eq. 45
k	--	Karman's constant (≈0.4 for open channel flow)
k_c	--	mass transfer coefficient (cm/sec)
K	--	mass transfer rate constant defined by Eq. 50
L	--	thickness of carbon-filled packet or panel
ℓ	--	distance from the deepest part of a channel to the furthest bank
$m_{p,w}$	--	mass of packet (p) or mass of water displaced (w)
M	--	amount of material discharged in a spill
N	--	number of packets
n	--	number of cycles; used as a summation index in Eq. 49
ΔP	--	pressure difference
$\overline{Q}$	--	volumetric discharge rate relative to carbon panels
q	--	concentration of adsorbed maerial on solid phase (moles/mass)
R	--	hydraulic radius
Re	--	Reynolds number ($d_p v\rho/\mu$), dimensionless
Re'	--	Reynolds number for packed bed ($d_p \overline{U}_a \rho/\mu\theta$), dimensionless
S	--	slope of the channel floor (the slope of the energy grade line)
Sc	--	Schmidt number ($\nu/\mathcal{D}$), dimensionless
t	--	time
$\hat{t}$	--	elapsed time following the arrival of fluid particle ($t - \frac{x}{v_s}$)
$\overline{U}_a$	--	superficial flow velocity, the average linear velocity through a bed computed on the basis of the empty cross-sectional area
u_*	--	shear velocity, = $(\tau_0/\rho)^{1/2}$ (also see Eq. 32)
V	--	volume
V_p	--	volume of a packet

$v, \bar{v}$ -- velocity, cross-sectional area mean

v_s -- slip velocity, the velocity difference between an object and the fluid in which it is suspended

v_t -- terminal velocity

W -- width of a watercourse

x -- distance, as defined where used

y, y' -- distance, as defined where used

Z -- defined as $(v_t/ku_*\beta)$, Eq. 30

z -- distance, as defined where used

Greek Letters

β -- proportionality constant $(\varepsilon_d/\varepsilon_s)$

ε_d -- eddy diffusion coefficient of liquid

ε_s -- eddy diffusion coefficient of solids suspended in turbulent flow

$\varepsilon_{y,z}$ -- eddy diffusion in y and z direction, respectively

η -- relative number of packets suspended in a watercourse between two arbitrary depths (see Eq. 31)

θ -- packed bed void fraction or void space

μ -- viscosity

ν -- kinematic viscosity (μ/ρ)

ξ -- defined by Eq. 14

ρ -- density of fluid

ρ_p, ρ_b -- density of packet, bulk density of adsorbent (carbon)

$\tau_o, \tau_{y'}$ -- shear stress at point o (wall) and at point y', respectively

ϕ -- phenol

ψ -- fraction of flotation material in a packet (1 - ψ = fraction of carbon)

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SUMMARY

An analysis was made of the feasibility of using activated carbon adsorbent in packets and panels to clean up water-soluble hazardous material spills in surface waters.

A model for the containers is given in which movement of fluid through the packets is created by buoyancy forces and turbulence and through panels by causing them to lag the flow velocity of the waterway. Mass transfer to the carbon particles from the low-velocity fluid passing through the containers was assumed to be controlled by the fluid-side resistance.

Equations were derived to describe the removal of dissolved pollutants from water by buoyant packets that were either (a) cycled through a water column, or (b) suspended in the waterway by natural turbulence. Cycling consisted of injecting packets of adsorbent at the bottom of a water column, allowing them to float to the surface where they would be retrieved, and reinjecting them at the bottom of the water column. The reduction of pollutant concentration in volume V from C_o to C by N packets of fresh adsorbent in n cycles is given by

$$\ln \frac{C}{C_o} = - \frac{Nn}{V} \left\{ \frac{D}{v_t} \overline{U}_a A_p \left[1 - \exp \left(- \frac{k_c a L}{\overline{U}_a} \right) \right] + V_p \theta \right\} .$$

Calculations based on the above equation using phenol as a model pollutant and a carbon-phenol ratio of 10 indicate that the packet cycling approach is inefficient. The calculations considered packets with a 10.2-cm by 10.2-cm (4-in by 4-in) cross-section, thicknesses of 1.27 cm (0.5 in) and 0.64 cm (0.25 in), and carbon particle sizes of 0.12 cm and 0.06 cm. Pumping requirements for packet injection at the bottom of the water column were found to exceed by 5 to 11 times (at a minimum) the volume of fluid that would be pumped if a packed column of carbon were used for fluid cleanup. Calculations performed for representative waterways reveal water-soluble spills are rapidly diluted by turbulent mixing and longitudinal dispersion. Dilution increases the volume of fluid, V, to be treated and as shown by the equation, will increase the number of packet-cycles needed to effect a fixed fractional reduction in pollutant concentration. Reasonable estimates of the cycling time and the large number of cycles required indicate that the process is inherently slow and usually incapable of lowering the pollutant concentration in a waterway as rapidly as can longitudinal dispersion.

Consideration of pollutant removal by fresh buoyant packets suspended in turbulent waterways for a time t yields

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$$\ln \frac{C}{C_o} = - \frac{\bar{U}_a A_p N t}{V} \left[1 - \exp \left(- \frac{k_c a L}{\bar{U}_a} \right) \right] .$$

Plots of computed values of $\ln C/C_o$ versus t are given for various packet buoyancies using phenol as a model pollutant and a carbon-phenol ratio of 10. Comparisons are made with experimental data from the literature.

A study of the literature on sediment suspension and turbulence in waterways indicates that natural turbulence in most waterways is insufficient to suspend the buoyant packets with any degree of uniformity throughout the depth of the waterway. Even packets with the lowest buoyancy force for which calculations were made will concentrate near the water surface. Information on the suspension of objects of the size of the packets contemplated in this study is unavailable; the scale of the waterway turbulence could impose an upper limit on the size of an object that can be suspended. No estimate can be made at present of the increase in suspension time likely to occur as a result of buffeting of the rising packets by turbulence.

An equation was also obtained for adsorption of dissolved pollutants from water by adsorbent-filled panels hanging in waterways. For a waterway discharge rate of $\bar{Q}$ relative to the panels and a total panel area normal to the flow, A_c, the equation is

$$\ln \frac{C}{C_o} = - \frac{A_c \bar{U}_a}{\bar{Q}} \left[1 - \exp \left(\frac{k_c a L}{\bar{U}_a} \right) \right] .$$

A plot is given of computed values of percent phenol removed versus the relative discharge rate with spill size appearing as a parameter. As seen from the equation, the fraction of pollutant removed decreases as the relative discharge rate $\bar{Q}$ is increased. For a discharge rate of 25 m^3/sec (3000 ft^3/sec), about 5% (at most) of a 1814-kg (4000-lb) spill of phenol can be removed by carbon panels with a carbon-phenol ratio of 10. For large nonimpoundable waterways, i.e., discharge rates in excess of 850 m^3/sec (30,000 ft^3/sec), about 5% (at most) of an 18,140-kg (40,000-lb) spill can be removed by 181,400 kg (400,000 lbs) of carbon panels even with a fast response to a spill.

The computed performance of packets and panels given in this study are probably higher than can be attained in practice. The reasons for this are:

a. The assumption that packets and panels are always turned broadside to the flow

b. The neglect of flow resistance offered by the fabric that would be used to encase the adsorbent

c. The assumption of negligible resistance to mass transfer in the solid-phase and the assumption of equilibrium concentration at the external fluid-solid interface

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d. The assumption that fluid leaving a packet or panel is well mixed with the surrounding fluid in the waterway before entering another packet or panel

e. The assumption that adsorbent particles in the packets and panels will remain distributed in a uniform bed thickness over the entire cross-section

The rapid dilution of water-soluble spills by turbulent mixing and longitudinal dispersion will make the removal of even a few percent of the dissolved pollutant by carbon-filled panels unlikely in large, nonimpoundable waterways, unless the spill is massive.

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SECTION 1

INTRODUCTION

A growing, modern industrial society requires and produces many chemicals that can threaten public health and safety if discharged into waterways in sufficient quantities. In the course of production, transportation, storage, and utilization of these materials, some accidental spillage is certain to occur, and some fraction of this spillage will enter watercourses. Recent barge accidents on the Ohio and Mississippi Rivers have highlighted these threats and the need for an operational system to remove spilled, water-soluble organic hazardous materials from large, nonimpoundable waterways.

Activated carbon in one form or another (packaged or loose, floating or sinking in water, powdered, granular, and fibrous) has been proposed for adsorbing spilled, water-soluble hazardous organics from watercourses. Limited laboratory experiments and small field tests have been conducted with carbon to determine its spill cleanup potential (Refs. 1, 2, 3, 4, and 5). The results of these studies have been mixed, but as expected, activated carbon was shown to remove dissolved organic substances from water. These studies do not make clear, however, whether the use of carbon-filled packets and panels or loose carbon to clean up spills in large, nonimpoundable watercourses is technically or economically feasible.

Before further developmental work in this area was funded, a brief feasibility study was conducted of the various in-situ approaches to the removal of water-soluble, hazardous organics from nonimpoundable watercourses by means of carbon adsorption. The study was to concentrate on the adsorption process and to ignore related steps such as the harvesting or retrieval of the carbon-filled packets and carbon regeneration. Accordingly, it was the objective of this study to determine the rate of removal of dissolved pollutant and the percent of dissolved pollutant likely to be removed by using activated carbon under the best possible conditions. Based on these determinations, a recommendation was to be made on the matter of future funding of work in this area.

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SECTION 2

CONCLUSIONS

1. Buoyant packets of 0.64-cm (0.25-in) thickness injected into quiescent water will require pumping in excess of 5 to 11 times more fluid than necessary when using a packed column of carbon. For 1.27-cm (0.5-in) -thick packets, 7 to 14 times more fluid will be pumped than required for a packed column.

2. Buoyant packets are ineffective for removing spills of dissolved hazardous materials from waterways. The reasons for this are:

   a. The rapid dilution of spills in navigable waterways increases the number of cycles required to effect a fixed percentage of reduction in pollutant concentration.

   b. Reasonable estimates of the cycling time and the large number of cycles required indicate the process is inherently slow.

   c. Large volumes of fluid-packet mixtures must be pumped.

3. Natural turbulence in representative waterways does not appear to be sufficient to suspend buoyant packets with any uniformity throughout the depth of the waterway. No estimate can be made at present of the increase in suspension time likely to occur as a result of buffeting of the rising packets by turbulence.

4. Carbon-filled panels hanging in waterways appear to hold more promise for the removal of dissolved hazardous materials than do buoyant packets.

5. The percent of dissolved material that can be removed by panels decreases with an increase in discharge rate of the waterway and increases with the amount of carbon used.

6. For large, nonimpoundable waterways, i.e., discharge rates greater than 850 m^3/sec (30,000 ft^3/sec), carbon-filled panels become ineffective. The reasons for this are:

   a. Rapid dilution of water-soluble spills as large as 18,140 kg (40,000 lbs) to the point where treatment by any means would be difficult

   b. Under the best circumstances, with a rapid response less than 5% of an 18,140-kg (40,000-lb) spill of phenol will be recovered by

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181,400 kg (400,000 lbs) of carbon panels.

7. Turbulent diffusion and longitudinal dispersion in waterways will rapidly dilute water-soluble spills to the point where treatment by any means will be extremely difficult. Spills of 1814 kg (4000 lbs) or less in waterways of discharge greater than about 35.4 m^3/sec (1250 ft^3/sec) will probably dilute to less than 4 ppm within 8 hours, spills of 18,140 kg (40,000 lbs) or less in waterways of discharge greater than about 990 m^3/sec (35,000 ft^3/sec) will probably dilute to less than 4 ppm within 8 hours.

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SECTION 3

RECOMMENDATIONS

Panels and buoyant packets filled with activated carbon or other adsorbent should not be considered for the removal of water-soluble spilled materials from nonimpoundable waterways unless the spill is massive with respect to the volumetric flowrate of the waterway and the adsorbent can be applied very soon after the spill.

Proposed approaches involving the application of in-situ adsorbents for the removal of water-soluble hazardous material spills from waterways should be examined in light of the results of this feasibility study. Regardless of the quality of an adsorbent or its specificity for the spilled compound, the problems to be addressed are: (a) the rate of mass transfer to the adsorbent, (b) the very rapid longitudinal dispersion of dissolved substances in waterways, and (c) the removal of the spent adsorbent from the waterway.

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SECTION 4

ANALYSIS

ADSORPTION MODEL BASICS

Packets or panels of carbon granules will be considered to behave as fixed-bed adsorbers with a very small thickness; the carbon will adsorb dissolved organic material only from fluid that is inside the packet (either stagnant or flowing through). Packets of carbon merely immersed in fluid, with no flow of fluid through them, will adsorb organic material only from the stagnant liquid in the void space of the packet. To work most efficiently, fluid must flow through the packet. Fluid will flow through porous packets in response to a pressure difference, ΔP, across the packets. This ΔP will occur as a result of differences in velocity between the packet and the surrounding fluid and will be proportional to $\rho v^2/2$ (the proportionality factor iscalled a drag coefficient or a friction factor).

In a watercourse, differences in velocity between packets and the fluid will occur quite naturally as the packet is "dragged" along by the flow. By causing packets to lag the flow either by anchoring them in place or somehow increasing their drag, one can obtain various flowrates through them. A velocity difference between the packet and the surrounding liquid can also be obtained by employing packets with a density different from that of water. The buoyancy force will induce the packets to rise or fall through a water column and accelerate to some velocity (terminal velocity) where the frictional drag force on the packet equals the buoyancy force.

The properties of carbon used in the computations made for this study are given in Appendix A.

A force balance can be written for an object rising through a column of liquid

$$m_p \frac{dv}{dt} = (m_p - m_w)\, g - f \frac{\rho v^2}{2} A_p, \qquad (1)$$

where m_p is the mass of a packet and m_w the mass of water displaced by the packet, A_p is the cross-sectional area of the packet normal to the flow direction, and g is the acceleration due to gravity (the definitions of the symbols are given in the list of abbreviations and symbols). At steady state, when the terminal velocity is attained, $dv/dt = 0$. Making this substitution in Eq. 1 and letting $m_p - m_w = (\rho_p - \rho)V$, the terminal velocity, v_t, is found to be

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$$v_t = \left(\frac{2g(\rho_p - \rho)}{\rho} \frac{V}{A_p f} \right)^{1/2} . \qquad (2)$$

The friction factor, f, is related to the shape of the object moving through the fluid, or V/A_p, and to the Re. In many engineering texts, Eq. 2 is written with V/A_p given for a sphere and the f vs Re correlation given as a function of a shape factor, or, sphericity to compensate for the assumed ratio V/A_p of 4d/3. For details on this approach, the reader is referred to Brown and Assoc. (Ref. 6).

A general review of settling velocities of particles (the same as particle rising velocities only the buoyancy has a different sign) that also discusses friction factors (or drag coefficients) for various shapes is given by Graf (Ref. 7). For this feasibility study it was assumed that the thin, rectangular-shaped packets would pass through the water with the large rectangular face oriented normal to the flow direction. According to Brown (Ref. 6), particles will tend to move in a manner that offers greatest resistance. In agreement with this general statement are the experiments reported by Graf (Ref. 7) which indicated that at Re numbers outside the Stokes range, elongated bodies will orient themselves broadside to the relative motion.

Flow velocities through the porous packets can be computed by using standard calculational procedures for single-phase flow through packed beds. The needed equations and dimensionless plots are available in many texts (e.g., Ref. 8). An equation relating the pressure drop across a packed bed to flow velocity through the bed can be written as

$$\overline{U}_a = \left(\frac{2\ g\ d_p\ \Delta P}{F_j\ f\ L \rho} \right)^{1/2} , \qquad (3)$$

where $\overline{U}_a$ is the superficial velocity (the linear velocity of the fluid through the bed computed on the basis of the total or empty cross-sectional area), F_j and f are friction factors related to the bed porosity, the carbon granule sphericity, and the Re number written as $d_p F_{Re} \overline{U}_a \rho/\mu$; the term F_{Re} is a factor used to modify d_p and is also a function of bed porosity and packing material sphericity. The trial and error solution for $\overline{U}_a$ using Eq. 3 and a plot of Reynolds number vs f for randomly packed particles (Ref. 8) converges rapidly.

The overall resistance to mass-transfer from the bulk liquid to the solid includes the resistive contribution of (a) the layer of solution around the particles, (b) diffusion of solute through pores within the particles, and (c) physical adsorption at active sites on the solid.

The mass-transfer coefficients from the bulk liquid to the exterior surface area of the carbon particles (step [a] above) were computed using general correlations obtained at low Re numbers (Ref. 9). For Re' from 0.08 to 125 (where $Re' = d_p \overline{U}_a \rho/\mu\theta$ and θ is the bed void fraction), the mass-transfer correlation used was

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$$\frac{k_c}{\overline{U}_a} (Sc)^{0.58} = 2.40 (Re')^{-0.66} . \quad (4)$$

The Schmidt number, Sc, is defined as $\nu/\mathscr{D}$. The diffusion coefficient, $\mathscr{D}$, for the organic compound being adsorbed from the water phase can usually be computed with fair accuracy using available methods (Refs. 10 and 11).

for steady-state mass-transfer from the water phase to the carbon, and piston flow through the packed bed (or packet),

$$-\overline{U}_a dC = k_c a (C-C_i) dx , \quad (5)$$

where a is the total exterior particle surface area for mass transfer per unit volume of packed space. For spheres,

$$a = \frac{6}{d_p} (1-\theta) (1-\psi) , \quad (6)$$

where θ is the bed void fraction and ψ is the fraction of flotation material in the packet.

Values of k_c obtained from Eq. 4 are applicable to the layer of solution surrounding the particle. Evaluation of C_i, the concentration of solute at the exterior particle-liquid interface, may involve the addition of equations describing the rate of diffusion through the pores interlacing the solid and the rate of physical adsorption. Ultimately, C_i would be related to the concentration of solute at active adsorption sites on the carbon solid.

The assumption will be made that the resistance offered by the pore diffusion and physical adsorption steps is very small relative to the resistance to mass transfer from the bulk liquid to the exterior surface of the carbon. Therefore, C_i can be closely approximated as the concentration of the solute in equilibrium with the solid, i.e., the solute concentration given by an experimentally determined adsorption equilibrium isotherm. The adsorption equilibrium isotherm could be used to relate C_i to the bulk fluid concentration, C, via a material balance if the initial moles of solute and the mass of carbon were known. Since the carbon packets considered in this study are fairly thin, and the packets moving through the liquid may have fluid passing through them in either direction depending on which of the two broad sides are facing the flow, C_i will be assumed to be constant for all carbon granules and hence independent of distance, x, through the packet. C_i will vary with time as the concentration of organic material on the carbon increases. At any particular time, the change in concentration across a packet is given by integrating Eq. 5 from 0 to L and C_{in} to C_{out} to yield

$$\frac{C_{out} - C_{in}}{C_{in}} = \left(1 - \frac{C_i}{C_{in}}\right) \left[1 - \exp\left(-\frac{k_c a L}{\overline{U}_a}\right)\right] . \quad (7)$$

For fresh activated carbon, C_i is negligible for many organics and Eq. 7 can be written as

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$$\frac{C_{out}}{C_{in}} = \exp\left(-\frac{k_c aL}{\overline{U}_a}\right). \quad (8)$$

Equations 7 or 8 indicate the change in solute concentration occurring in fluid passing through the packed bed. The fraction of pollutant removed from water passing through a fresh carbon packet is

$$\frac{C_{in} - C_{out}}{C_{in}} = 1 - \exp\left(-\frac{k_c aL}{\overline{U}_a}\right). \quad (9)$$

ANALYSIS OF POLLUTANT REMOVAL BY BUOYANT PACKETS

Buoyant Packet Cycling

It has been suggested that watercourses or lakes polluted by spills of water-soluble hazardous organic compounds could be cleaned up faster or more efficiently if packets of activated carbon adsorbent were used. These packets would be fabricated in sizes small enough to be mixed with water and injected at the bottom of a polluted volume of water by a solids-handling pump, and buoyant enough to rise through the polluted water at some known terminal velocity. The movement of the packet upward through the water would enhance mass transfer of the pollutant to the carbon, as described earlier. Upon arrival at the water surface, the packets would be automatically gathered and pumped down to the bottom of the water column again to start another cycle.

For this study, a packet size of 10.2 cm by 10.2 cm (4 in by 4 in) with a thickness of either 1.27 cm (0.5 in) or of 0.64 cm (0.25 in) was chosen. Packet buoyancy was assumed to be provided by adding foamed plastic particles with a specific gravity of 0.2 to the carbon granules used to fill the packets. The foamed plastic would have a size equal to the carbon granules used. Calculations were performed for carbon granules with a diameter of 0.12 cm and 0.06 cm (14 and 28 mesh).

For the purpose of this feasibility study, the buoyant-packet-cycling approach was assumed to be used to clean up 3785 m^3 (10^6 gal) of water contaminated with 100 ppm of phenol. A carbon-to-phenol ratio of 10 was assumed.

Using the equations and procedures outlined in the previous pages, values of ρ_p, ΔP, gm carbon/packet, $\overline{U}_a$, and k_c were calculated for terminal rise velocities of 3.8, 7.62, 15.2, and 22.9 cm/sec (0.125, 0.25, 0.50, and 0.75 ft/sec) for carbon spheres with d_p = 0.12 cm and 0.06 cm, a packet thickness, L, of 1.27 cm (0.5 in) and 0.64 cm (0.25 in), and a packet void fraction, θ, of 0.39. The relevant calculated results are given in Table 1. At v_t = 30.5 cm/sec (1.0 ft/sec), the required buoyancy dictates that the packets have a density of 0.29 gm/cc; this density cannot be attained using flotation particles with a density of 0.20 gm/cc. A packet composed entirely of flotation particles with ρ = 0.2 and θ = 0.39 would have a density of 0.512 gm/cc.

TABLE 1. SUMMARY OF CALCULATED MASS-TRANSFER INFORMATION FOR BUOYANT PACKETS

d_p (cm)	L (cm)	ΔP (Pascals)	v_t (cm/sec)	ρ_p	% Carbon in Packet, 100 $(1-\psi)$	$\frac{\text{Carbon}}{\text{Packet}}$, (gm)	N	$\bar{U}_a$ (cm/sec)	$k_c \times 10^3$ (cm/sec)
0.12	1.27	1.058	3.81	0.9916	68.34	40.84	92,700	0.0115	0.914
0.12	1.27	4.405	7.62	0.9648	64.54	38.55	98,200	0.0466	1.457
0.12	1.27	18.58	15.2	0.8508	48.29	28.85	131,200	0.201	2.37
0.12	1.27	47.32	22.9	0.620	15.38	9.19	411,800	0.498	3.21
0.12	0.64	0.800	3.81	0.9871	67.73	20.23	187,100	0.0172	1.02
0.12	0.64	3.31	7.62	0.9468	61.98	18.51	204,500	0.0705	1.64
0.12	0.64	15.46	15.2	0.7516	34.15	10.20	371,100	0.329	2.78
0.06	1.27	1.058	3.81	0.9916	68.34	40.84	92,700	0.00262	0.8788
0.06	1.27	4.405	7.52	0.9648	64.54	38.55	98,200	0.01117	1.438
0.06	1.27	18.58	15.2	0.8508	48.29	28.85	131,200	0.0481	2.363
0.06	1.27	47.32	22.9	0.620	15.38	9.19	411,800	0.1244	3.264

A packet rising through the water column of depth D at velocity v_t will treat $\bar{U}_a A_p D/v_t$ units of water. The fraction of phenol removed from the water passing through a packet is given by Eq. 9. Thus, the amount of phenol removed from the water by N packets of fresh carbon after one pass through a depth D at v_t is given by the equation

$$V\Delta C = \frac{D}{v_t}\ \bar{U}_a A_p NC\ \left[1 - \exp\left(-\frac{k_c aL}{\bar{U}_a}\right)\right]. \qquad (10)$$

Equations 9 and 10 were used to compute the values given in columns 4 and 5 of Table 2. A depth, D, of 3.05 m (10 ft) was chosen for this exercise.

As the packets float on the water surface prior to gathering and returning them to the river bottom, the carbon will adsorb phenol from the fluid remaining in the void space of the packets. To account for this adsorption, it has been assumed that for each cycle, in addition to the pollutant adsorbed while rising through the water, the carbon in a packet will remove enough phenol to attain equilibrium with a volume of phenol-water mixture sufficient to occupy the packet void space, that is, $(C-C_i)NV_p\theta$. Thus, the total amount of phenol removed per cycle is given by adding this quantity to Eq. 10. The result of this addition for fresh carbon ($C_i \approx 0$) is given in column 6 of Table 2.

The total number of cycles, n, required by fresh carbon packets to remove a given fraction of the phenol (or any pollutant) can be found from Eq. 11.

$$\ln\frac{C}{C_o} = -\frac{Nn}{V}\left\{\frac{D}{v_t}\ \bar{U}_a A_p\left[1 - \exp\left(-\frac{k_c aL}{\bar{U}_a}\right)\right] + V_p\theta\right\}. \qquad (11)$$

The total time required to reduce the phenol concentration from C_o to C is primarily a function of the packet retrieval time, the solids-handling pump capacity, and the number of cycles, n. According to Eq. 11, if N should be increased, the number of packet-cycles will be unaffected. This is true for fresh carbon packets only (the restrictions under which Eq. 11 was derived). Thus, to complete the desired cleanup job, the same number of packets would have to be retrieved and pumped to the bottom of the water column. The volume of fluid-solids handled by the recycling pump, using a 15% maximum solids loading as typical, is $NnV_p/0.15$.

Assuming a sufficiently high carbon-phenol ratio, Eq. 11 was used to determine Nn for 90% removal of phenol for 3785 m^3 (10^6 gal) of water. The estimated volume to be pumped is given in column 10 of Table 2. The computed values, ranging from 3.71×10^4 to 10.5×10^4 m^3 (9.8×10^6 to 27.7×10^6 gal), though undoubtedly an underestimate, greatly exceed the amount of pumping required if a packed carbon bed were used to remove the phenol. If the purified water exiting the carbon bed was continually dumped back and mixed with the contaminated water, the pump would be required to handle about 8710 m^3 (2.3×10^6 gal) to reduce 3785 m^3 (10^6 gal) of water from 100 ppm to 10 ppm. If, however, the purified water was not returned to the reservoir, only 3407 m^3

TABLE 2. SUMMARY: CALCULATED VALUES FOR BUOYANT PACKET CYCLING

d_p (cm)	L (cm)	v_t (cm/sec)	$\left(1 - \frac{C_{out}}{C_{in}}\right)$	$\frac{gm\ \phi}{pass}$	Total $\frac{gm\ \phi}{cycle}$	$\frac{\%\ \phi}{cycle}$	Packet x passes remove 80% ϕ (10^7)	Pumping,(1) Remove 80% ϕ (10^4 m^3)	Est. Pumping(1,2) Remove 90% ϕ (10^4 m^3)
0.12	1.27	3.81	0.8781	773.1	1247	0.3294	5.65	4.94	5.68
0.12	1.27	7.62	0.5406	1021.5	1524	0.4025	4.90	4.28	4.92
0.12	1.27	15.2	0.1979	1078	1749	0.462	9.87	4.95	5.72
0.12	1.27	22.9	0.0377	1064	3169	0.8372	12.89	8.63	9.92
0.12	0.67	3.8	0.5406	1437	1915	0.5058	7.426	3.24	3.72
0.12	0.67	7.62	0.2436	1450	1973	0.5211	7.88	3.44	3.94
0.12	0.67	15.2	0.0544	1371	2320	0.6128	12.16	5.31	6.09
0.06	1.27	3.81	≃ 1	200.8	675	0.178	10.9	9.54	10.5
0.06	1.27	7.62	0.9984	452	953	0.2517	7.82	6.85	7.84
0.06	1.27	15.2	0.8408	1096	1767	0.4667	5.66	4.96	5.64
0.06	1.27	22.9	0.2686	1894	3999	1.056	7.83	6.85	7.84

(1) Assuming 15% of the volume pumped consists of packets.

(2) Assuming sufficient carbon to make C_i negligible (probably carbon/ϕ = 20 to 30).

(0.9×10^6 gal) would have to be pumped.

Numerical solutions of the mass transfer equations for a carbon-phenol ratio of 10 (using values of C_i determined from an adsorption isotherm for phenol and Nuchar C-190 given in Figure A-1 in Appendix A) obtained for 80% removal of phenol from a mixture with an initial concentration of 100 ppm phenol, are given in columns 8 and 9 of Table 2. The adsorption isotherm and the carbon-phenol ratio of 10 will not permit more than about 84.7% of phenol to be removed without regeneration of the carbon. The results of these calculations are also plotted in Figure 1 as pumping volume required versus the terminal rise velocity of the packets.

A reduction in carbon particle size results in greater resistance to flow through the packet and, hence, a lower value of $\overline{U}_a$. The lower value of $\overline{U}_a$ and the greater area per unit volume, a, afforded by the smaller particles increases the percentage of phenol removed from the fluid passing through the packet. The net effect of using the smaller particle size, as shown in Figure 1, is to slightly raise and shift the minimum of the curve toward higher terminal rise velocities. A decrease in the packet thickness from 1.27 to 0.64 cm (0.5 to 0.25 in) increases the number of packets (since the carbon-phenol ratio is assumed to be fixed at 10), offers less resistance to flow through the packet, and causes the water pumping minimum to shift toward smaller terminal rise velocities. Thinner packets appear to require fewer total packet passes, Nn, through the water column to adsorb the same amount of phenol.

The calculations do not include a flow resistance for the fabric casing or container for the carbon and flotation granules comprising the packets. Smaller particle sizes will require a tighter fabric weave to contain the particles while decreasing the packet thickness will enhance the importance of the contribution of the fabric to the overall resistance to flow through the packet. For a fixed amount of carbon, halving the packet thickness will more than double the number of packets, since the resistance to packet movement upward through the water changes very little and maintaining the buoyancy force constant requires that the percentage of flotation in thinner packets be increased. The greater number of packets means larger packaging costs. No consideration has been given here to the problem of how to construct or fabricate a packet, so as to keep the carbon-flotation granular mixture uniformly distributed throughout the thin packets rather than lumping all together on one side or corner of the packet to give a sacklike appearance.

Buoyant Packets Suspended in Turbulent Rivers

If buoyant packets, considered for nonflowing water bodies in the previous pages, were injected into a turbulent river, the random buffeting of the packets by the eddies will increase the immersion time. It has been suggested that a sufficiently high level of river turbulence would result in the packets remaining suspended in the water indefinitely. An analysis will be made and equations derived to describe the rate of adsorption of dissolved materials by buoyant packets of activated carbon suspended in a watercourse. This will be followed by a discussion of river turbulence and the suspension of solids.

To remain suspended in a river, a packet must encounter a net downward

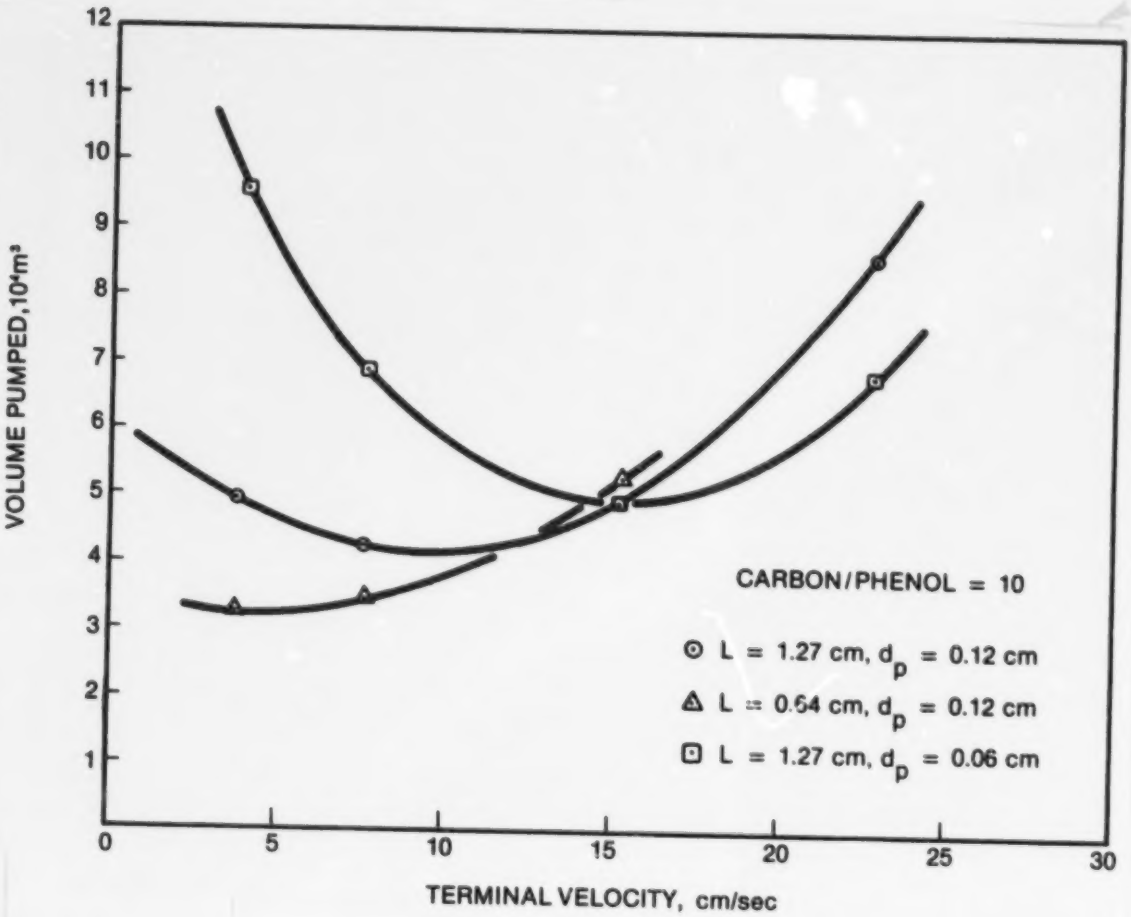
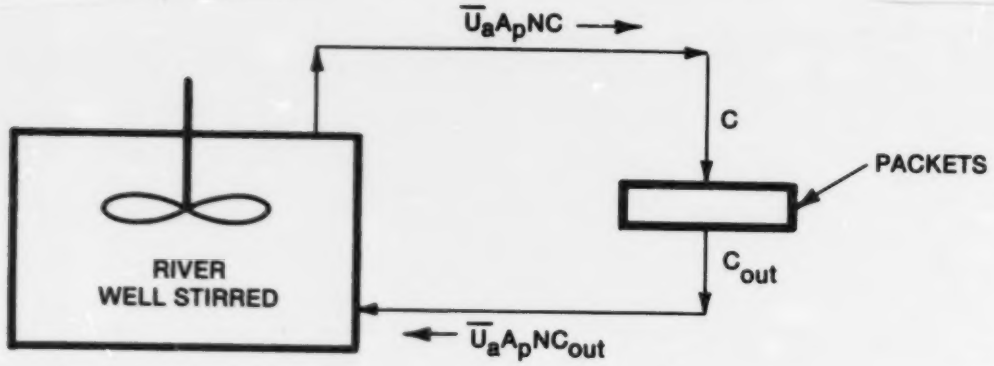


Figure 1. Fluid pumping required to remove 80% Phenol from 3785 m^3 (10^6 gal) with buoyant carbon packets (10.2 cm x 10.2 cm x L)

force of sufficient strength to counter the steady, buoyant force. It is assumed that suspension occurs when the average slip velocity (the velocity of the fluid relative to the packet) is equal to the terminal rise velocity of the packet. As in the previous section, it is assumed that the packet will be oriented broadside to the flow. Fluid entering each packet is assumed to be well mixed and hence representative of the river in the surrounding vicinity. Fluid exiting a packet is assumed to mix very rapidly with the surrounding fluid. Figure 2 shows a simple schematic to illustrate the adsorption model. The change in concentration of solute in the well-stirred river is equated to the rate at which the solute is removed by the packets. The fluid feed rate to the packets is $\overline{U}_a A_p N$ and the fraction of solute removed from the fluid by fresh, activated carbon packets is given by Eq. 9. The differential equation for this case is



$$-V\frac{dC}{dt} = \overline{U}_a A_p NC\,(1 - C_{out}/C)$$

Figure 2. Model, buoyant packets suspended in turbulent river.

$$-V\frac{dC}{dt} = \overline{U}_a A_p NC\left[1 - \exp\left(-\frac{k_c aL}{\overline{U}_a}\right)\right] \tag{12}$$

or, separating variables and integrating,

$$\ln\frac{C}{C_o} = -\frac{\overline{U}_a A_p Nt}{V}\left[1 - \exp\left(-\frac{k_c aL}{\overline{U}_a}\right)\right] \tag{13}$$

or, simplifying,

$$\ln\frac{C}{C_o} = -\xi t. \tag{14}$$

The V in the denominator of Eq. 13 refers to the volume of water to be treated, and t is the time the packets remain in suspension.

Calculations of ξ were made for various terminal rise velocities and the packet and granule sizes investigated for quiescent water. All of the quantities required to determine ξ were calculated for packets in still water and appear in Tables 1 and 2. Values of ξ (hrs^{-1}) for the conditions cited above are tabulated in Table 3.

Equation 12 was solved numerically to obtain values of C/C_o as a function of t. When C/C_o is about 0.6 (for a carbon-phenol ratio of 10 and for the phenol adsorption isotherm used, Figure A-1), the concentration of phenol at the exterior surface of the particle becomes large enough to necessitate the use of numerical methods. The results of the numerical solutions for the rate of removal of phenol by packets suspended in a turbulent river are plotted in Figure 3.

TABLE 3. REMOVAL OF POLLUTANT BY SUSPENDED PACKETS (10.2 cm x 10.2 cm x L)

d_p (cm)	L (cm)	v_t (cm/sec)	$1 - \frac{C_{out}}{C_{in}}$	N	$\bar{U}_a$ (cm/sec)	ξ $(hrs)^{-1}$	Time (hrs) to remove 80% ϕ
0.12	1.27	3.81	0.8781	92,700	0.0115	0.0919	21.9
0.12	1.27	7.62	0.5406	98,200	0.0466	0.2428	8.10
0.12	1.27	15.2	0.1979	131,200	0.201	0.5124	3.92
0.12	1.27	22.9	0.0377	411,800	0.498	0.7589	2.67
0.12	0.64	3.81	0.5406	187,100	0.0172	0.1708	11.76
0.12	0.64	7.62	0.2436	204,500	0.0705	0.3448	5.83
0.12	0.64	15.2	0.0544	371,100	0.329	0.6521	3.08
0.06	1.27	3.81	1	92,700	0.00262	0.0239	84.27
0.06	1.27	7.62	0.9984	98,000	0.01117	0.1073	18.74
0.06	1.27	15.2	0.8408	131,200	0.0481	0.521	3.86
0.06	1.27	22.9	0.2686	411,800	0.1244	1.351	1.49

Since Eqs. 12 and 13 are quite similar to the equations derived for packets rising up through a quiescent pool (except for the term $V_p\theta$ for the adsorption of phenol from stagnant fluid in the void space of the packet), the plot of C/C_o against t reveals about the same information as given in Figure 1 regarding immersion times necessary to remove a fixed fraction of the phenol. The results show that at high terminal rise velocities the packets with the smaller carbon particles will remove phenol fastest, while at 3.81 cm/sec (0.125 ft/sec), the lowest terminal rise velocity for which calculations were made, the thin packet is faster.

The results shown in Figure 3 are independent of the spill size, or amount of water to be treated, as long as the water initially contained 100 ppm of phenol and the ratio of carbon to phenol is 10. If, for example, the initial concentration of phenol was 250 ppm, Eq. 13 indicates that the carbon packet concentration, N/V, would be 2.5 times greater than it would be for a 100-ppm phenol-water mixture to maintain a carbon-to-phenol ratio of 10. The information given in Figure 3 can be easily converted to 250-ppm phenol-water mixtures by merely dividing the time axis by 2.5. This has been done for the 1.27-cm (0.5-in) -thick packet with a 0.12-cm particle size in Figure 4 in order to compare these calculated results with experimental data reported by Calspan (Ref. 1). The carbon-filled bags used in laboratory channel tests conducted by Calspan (Ref. 1) were not suspended in the stream by turbulence, but were attached to floats and permitted to drift with the lab channel current. A comparison between the curves calculated for the carbon-flotation packet model and the lab channel tests indicates a combination of turbulence level and slip velocity between the stream flow and the carbon-filled bags in the Calspan

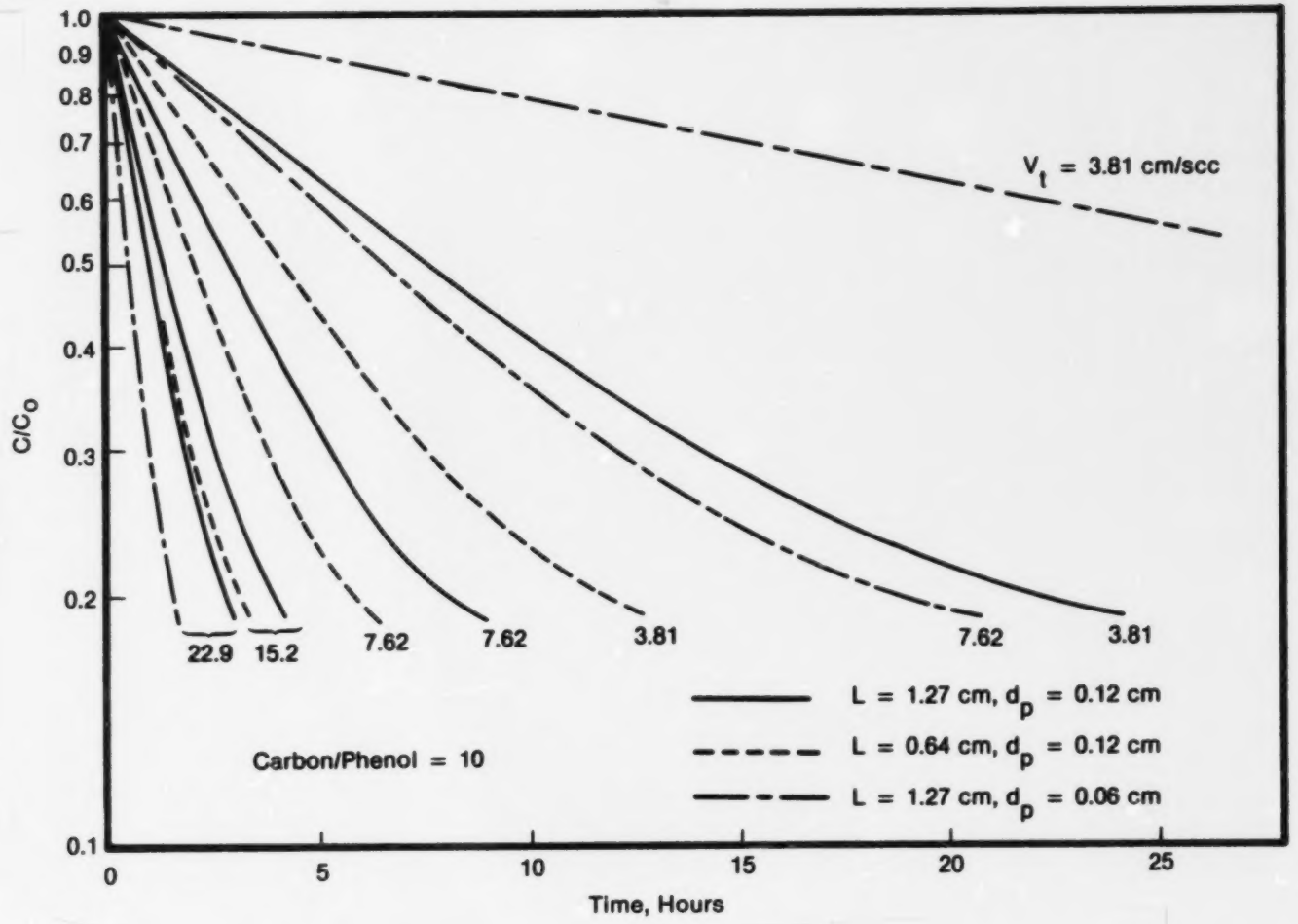


Figure 3. Computed removal of phenol by suspended buoyant packets of activated carbon (10.2 cm x 10.2 cm x L), C_o = 100 ppm

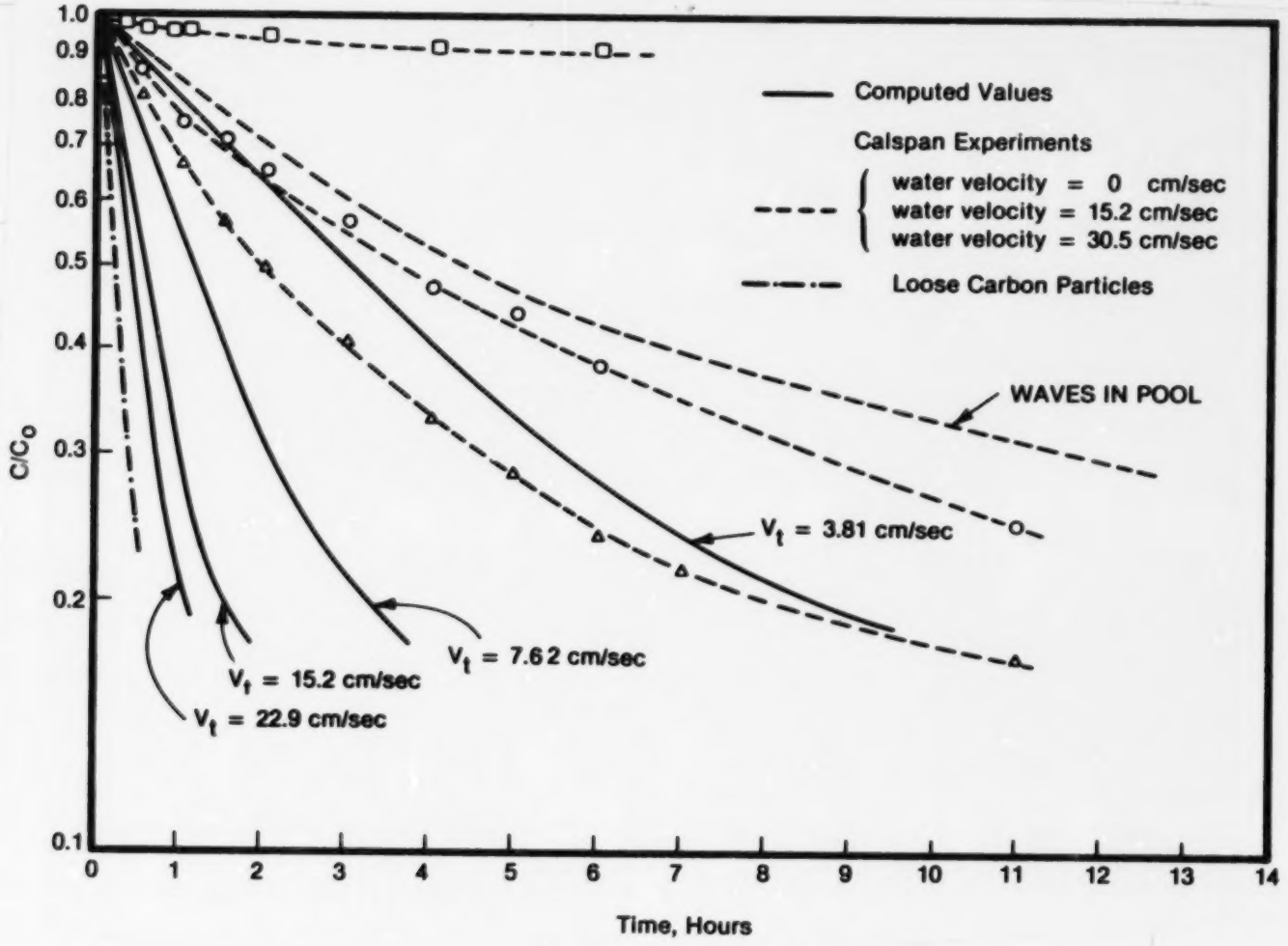


Figure 4. Removal of phenol by suspended buoyant packets of activated carbon (10.2 cm x 10.2 cm x 1.27 cm), C_o = 250 ppm, d_p = 0.12 cm.

channel tests equivalent to a slip velocity between 3.81 and 7.62 cm/sec (0.125 and 0.25 ft/sec) for the model. The difference in the shape of the curves is probably due to the difference in the phenol-carbon adsorption isotherm used and perhaps to some extent to the assumption that the pore diffusion term in the overall mass-transfer equation can be neglected for the small values of $\overline{U}_a$ encountered. Channel test results in which loose Aqua Nuchar carbon was applied to the phenol-water mixture (Ref.1) are also given in Figure 4.

River Turbulence and Packet Suspension

There is a moderately extensive literature on sediment transport in open-channel flow and the steady-state distribution of suspended matter in turbulent watercourses. None of the literature found, however, is concerned with objects the size of the buoyant carbon packets considered here or with objects that will float rather than sink (though the latter point is merely a matter of the sign on the velocity term). In the derivation of equations to describe the distribution of suspended solids in a turbulent flow, it is usually assumed that the effect of turbulence on the solids can be expressed by a diffusion-dispersion equation(the diffusional theories). Some derivations given in the literature are briefly outlined and discussed.

For incompressible fluids the continuity equation for mass transfer can be written as

$$\frac{\partial C}{\partial t} + v\cdot\nabla C - \mathscr{D}\nabla^2 C = 0. \qquad (15)$$

Equation 15 can be modified for a turbulent flow field by expressing the instantaneous values C and v in terms of the mean values $\overline{C}$ and $\overline{v}$ averaged over short time intervals at a given position, and C' and v', the fluctuating component, as given by

$$C = \overline{C} + C' \qquad (16)$$

$$v = \overline{v} + v'. \qquad (17)$$

Substituting Eqs. 16 and 17 into Eq. 15, and averaging each term over a short time interval, we obtain

$$\frac{\partial \overline{C}}{\partial t} + \overline{v}\cdot\nabla\overline{C} + \nabla(\overline{C'v'}) - \mathscr{D}\nabla^2\overline{C} = 0. \qquad (18)$$

The quantity $\overline{C'v'}$ can be written as

$$\varepsilon_d \frac{\partial \overline{C}}{\partial x_i} = -\overline{C'v_i'} = \varepsilon_d \nabla\overline{C}, \qquad (19)$$

where ε_d is the eddy diffusivity. Substituting Eq. 19 into Eq. 15 yields

$$\frac{\partial \overline{C}}{\partial t} + \overline{v}\cdot\nabla\overline{C} - \nabla(\varepsilon_d\nabla\overline{C}) - \mathscr{D}\nabla^2\overline{C} = 0. \qquad (20)$$

Since ε_d is usually much larger than the molecular diffusivity, $\mathscr{D}$, the last term on the left of Eq. 20 can be neglected.

To calculate the steady-state vertical distribution of suspended material in a turbulent stream, let $\partial\overline{C}/\partial t = 0$ and assume $\overline{C}$ varies only in the vertical direction, y, i.e., $\partial\overline{C}/\partial x = \partial\overline{C}/\partial z = 0$. The resultant equation is

$$v\frac{\partial\overline{C}}{\partial y} - \frac{\partial}{\partial y}\left(\varepsilon_d\frac{\partial\overline{C}}{\partial y}\right) = 0. \tag{21}$$

If $\overline{C}$, v, and ε_d in Eq. 21 refer to solids, v will be written as v_t, the terminal velocity (rising or settling depending on the sign), and ε_s can be substituted for ε_d. Making these substitutions and integrating Eq. 21 once, we obtain

$$v_t\overline{C} - \varepsilon_s\frac{\partial\overline{C}}{\partial y} - 0. \tag{22}$$

The relationship between the eddy diffusivity of fluid mass, ε_d, and solid particles, ε_s, is still the subject of debate. For the relationship

$$\varepsilon_s = \beta\varepsilon_d \tag{23}$$

it has been found that for fine particles $\beta \approx 1$, or, $\varepsilon_s \approx \varepsilon_d$, and for coarse particles $\beta < 1$, or, $\varepsilon_s < \varepsilon_d$. For details on the relationship between ε_s and ε_d and the turbulent diffusion of solids, the reader is referred to Hinze (Ref. 12) and Graf (Ref. 13).

If ε_s is independent of y, Eq. 22 can be integrated to obtain

$$\frac{\overline{C}}{\overline{C}_b} = \exp\left[-\frac{v_t(y'-b)}{\varepsilon_s}\beta\right], \tag{24}$$

where C_b is a reference concentration at distance b from the fluid surface, and y' is the distance from the fluid surface. Equation 24 may apply in certain specially designed tests (Ref. 13).

For non-uniform turbulence distribution in two-dimensional channels, the shear stress distribution is given by

$$\frac{\tau_{y'}}{\tau_o} = \frac{y'}{D} \tag{25}$$

and one can assume a logarithmic velocity distribution

$$-\frac{dv}{dy'} = \frac{1}{k(D-y')}\sqrt{\frac{\tau_o}{\rho}} = \frac{u_*}{k(D-y')}, \tag{26}$$

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where k is Karman's constant (for open channel flow, k = 0.4), and u_* is the shear velocity. The shear stress at y' in a turbulent flow is given by the equation

$$\tau_{y'} = - \rho \varepsilon_d \frac{dv}{dy'} . \tag{27}$$

Combining Eqs. 25, 26, 27, and 23, it is found that

$$\varepsilon_s = \beta k u_* (D-y') \frac{y'}{D} . \tag{28}$$

Substituting Eq. 28 for ε_s in Eq. 22 and separating variables, we obtain

$$\frac{d\bar{C}}{\bar{C}} = - \left(\frac{v_t}{k u_* \beta} \right) \frac{D}{y'} \frac{dy'}{(D-y')} . \tag{29}$$

The result of integrating Eq. 29 from b to y' is

$$\frac{\bar{C}}{\bar{C}_b} = \left(\frac{D-y'}{y'} \frac{b}{D-b} \right)^Z , \tag{30}$$

where $Z = v_t/(k u_* \beta)$.

A plot of Eq. 30 illustrating the vertical solids concentration distribution for various values of Z is given in Figure 5. It is quite obvious from Figure 5 that more uniform distributions of solids with depth require low values of Z. In addition, Eq. 30 unfortunately yields the solids distribution relative to some reference point, b, below the surface; it does not yield absolute solids concentrations unless the concentration is known at some reference point.

To ascertain the relative suspended particles load rate, or, for the problem of interest here, the relative number of packets suspended at various depths in the watercourse, it is necessary to multiply $\bar{C}$ by the water velocity as a function of vertical position and integrate over the vertical region of interest, that is,

$$n = \int_{y_1}^{y_2} \overline{Cu} dy . \tag{31}$$

The fraction of packets at any depth would then be $\overline{Cu} \nabla y / n$.

The relative distribution of solids in rivers as predicted by Eq. 30 requires that Z be known. Of the terms comprising Z, v_t can be assigned depending on the packet density, $k \approx 0.4$, β can be taken to be equal to 1 (though for large objects like packets this may be incorrect) and u_* is given by the relation

$$u_* = (g D_1 S)^{1/2} , \tag{32}$$

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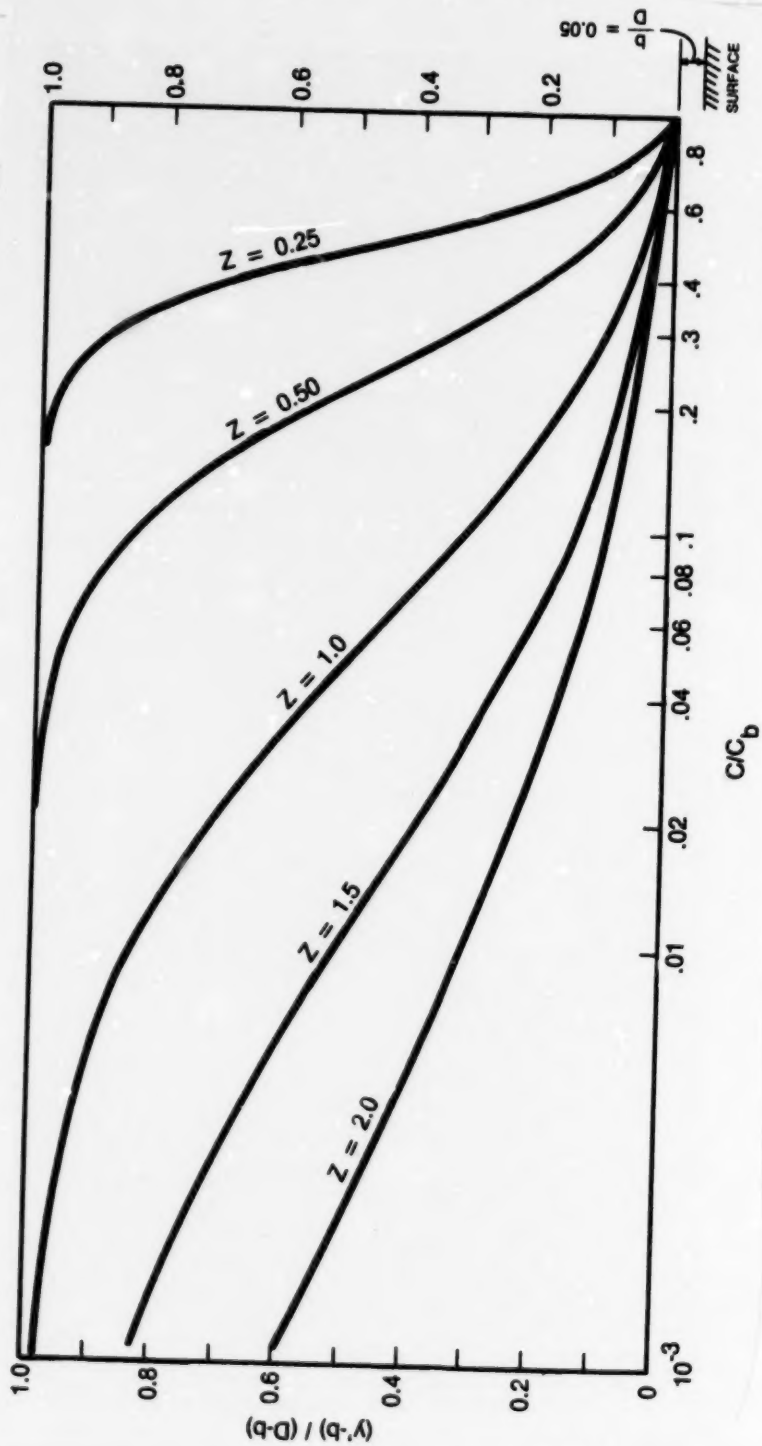

Figure 5. Distribution of buoyant suspended particles in waterways.

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where S is the slope of the channel bed and D_l is the hydraulic mean depth of the river. Values of Z for v_t = 3.81 cm/sec (0.125 ft/sec) and β = 1 are given in Table 4 for a number of rivers and waterways.

It would appear that even for low values of v_t, Z will be large enough to dictate that the vast majority of the packets will be in the upper 10% to 20% of the river depth. There is no information on the suspension of objects of the size of the packets; the scale of the river or channel turbulence could impose upper limits on the size of an object that can be suspended. In addition, there is evidence that the presence of suspended matter tends to dampen turbulence and smooth out the flow, hence reducing u_*, increasing Z, and causing the packet distribution shift upward to the river surface.

CARBON-FILLED PANELS HANGING IN RIVERS

Water-soluble pollutant spills can be removed from watercourses by panels packed with activated carbon hanging in the water flow in some homogeneous

TABLE 4. VALUES OF THE PARAMETER Z DETERMINED FOR VARIOUS WATERWAYS*

Waterway	$Z = \frac{v_t}{ku_*}$ (v_t = 3.81 cm/sec)
Chicago Sanitary & Ship Canal (Calumet Sag)	5.01
Missouri River (near Omaha, Nebraska)	1.24
Clinch River (near Clinchport, Virginia)	2.07
Copper Creek (near Gate City, Virginia)	0.92
Power River (Sneedville, Tennessee)	1.83
Coachella Canal (Holtville, California)	2.22
Bayou Anacoco	1.42
Nooksack River	0.36
John Day River	0.53
Sabine River	1.16
Green-Duwamish (Seattle, Washington)	1.94

* β assumed to be 1.0.

pattern downstream of the spill and turned broadside to the flow. The impact of the flowing water on the panels will provide the ΔP for flow through the porous panels and over the activated carbon granules.

Figure 6 illustrates the model for the use of carbon-filled panels in rivers. A material balance on a section dx of the watercourse festooned with panels yields

$$\theta v_s \frac{\partial C}{\partial x} + \rho_b \frac{\partial q}{\partial t} + \theta \frac{\partial C}{\partial t} = 0 , \tag{33}$$

where θ is the fraction of the river not occupied by carbon panels. For the carbon-phenol ratios used in this study, $\theta > 0.999$ and will be assumed to be unity. The term $\rho_b(\partial q/\partial t)$ describes the rate of accumulation of solute on the carbon and can be equated to the rate of mass transfer to the carbon-filled panels, that is,

$$\rho_b \frac{\partial q}{\partial t} = \overline{U}_a a_x (C - C_{out}) , \tag{34}$$

where a_x is the panel area available for flowthrough in the segment dx divided by the volume of the segment.

Using the transofrmation $\hat{t} = t - x/v_s$ and substituting Eq. 34 into Eq. 33, one obtains

$$- v_s \frac{\partial C}{\partial x} = \overline{U}_a a_x (C - C_{out}) . \tag{35}$$

The equations can be considered to describe a very loosely packed bed of adsorbers consisting of carbon-filled panels. Within each panel the concentration of adsorbed material on the carbon will be assumed to be uniform

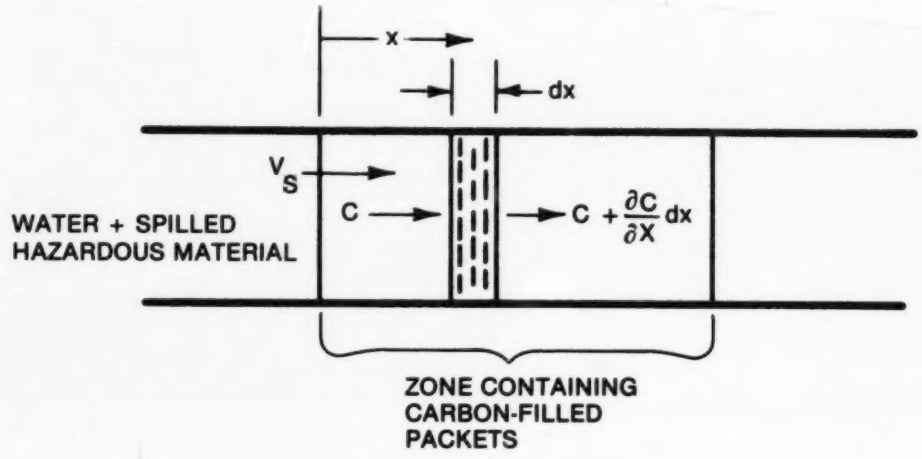


Figure 6. Watercourse with carbon-filled panels.

throughout the panel. Because the panels would be located at various distances downstream of a spill, the amount of pollutant adsorbed in a panel will depend on the location of the panel along the watercourse. As in a packed bed, the concentration of pollutant will be assumed to be constant over any cross-section normal to the flow.

Assuming fresh carbon (i.e., C_i is negligible), Eq. 35 can be written as

$$-v_s \frac{\partial C}{\partial x} = \bar{U}_a a_x C \left[1 - \exp \left(- \frac{k_c a L}{\bar{U}_a} \right) \right] . \qquad (36)$$

Separating variables and integrating, Eq. 36 becomes

$$\ln \frac{C}{C_o} = - \frac{\bar{U}_a A_t x}{v_s} \left[1 - \exp \left(- \frac{k_c a L}{\bar{U}_a} \right) \right], \qquad (37)$$

where A_t is the total panel cross-sectional area in a volume of the watercourse of length x. Equation 37 can be more conveniently written as

$$\ln \frac{C}{C_o} = - \frac{\bar{U}_a A_c}{\bar{Q}} \left[1 - \exp \left(- \frac{k_c a L}{\bar{U}_a} \right) \right], \qquad (38)$$

where $\bar{Q}$ is the volumetric discharge rate relative to the carbon panels and A_c is the total cross-sectional area of the panels in the watercourse.

With the simple treatment of the problem of relating q to C, it would not have been necessary to go through a more involved analysis starting with Eq. 33. If someone wished to deal with a situation requiring a more involved solid-liquid adsorption relationship for either carbon or ion-exchange resins, Eq. 33 and a suitably described relationship between q and C should aid in the analysis (Ref. 15).

Large-cross-section, thin panels hanging in a watercourse were assumed to have a drag coefficient equal to that obtained for flat plates, that is, $f = 2$ for $3000 < Re < 3.5 \times 10^5$ and $\Delta P = f \rho v_s^2/2$ (e.g., Ref. 7). This led to higher ΔP values for the panels than for rising packets at the same slip velocities. In addition, the panels contain only carbon; flotation is not required.

Table 5 contains relevant calculated values for panels of thickness 0.64 and 1.27 cm (0.25 and 0.5 in), filled with 0.12-cm or 0.06-cm-diameter granules. Some of the calculated results are plotted in Figure 7 as percent phenol removed per pass over the carbon panels vs $\bar{Q}$; the spill size in kilograms of phenol appears as a parameter and the carbon-to-phenol ratio is 10. The solid curves in Figure 7 are for a slip velocity of 30.5 cm/sec (1 ft/sec). For spills of 453.6 kg (1000 lbs) of phenol, dashed curves are given for slip

TABLE 5. SUMMARY OF MASS TRANSFER CALCULATION FOR HANGING CARBON-FILLED PANELS

d_p (cm)	L (cm)	v_s (cm/sec)	ΔP (Pascals)	$\bar{U}_a$ (cm/sec)	$k_c \times 10^3$ (cm/sec)	$\left(1 - \frac{C_{out}}{C_{in}}\right)$	$\bar{U}_a A_c \left(1 - \frac{C_{out}}{C_{in}}\right)$ (1) (ℓ/sec)
0.12	1.27	3.81	1.451	0.0149	1.003	0.9260	108.2
0.12	1.27	7.62	5.798	0.0609	1.619	0.6428	307.2
0.12	1.27	15.2	23.20	0.249	2.612	0.3340	652.2
0.12	1.27	22.9	52.19	0.537	3.393	0.2171	914.6
0.12	1.27	27.4	75.17	0.751	3.803	0.1781	1049
0.12	1.27	30.5	92.97	0.885	4.02	0.1613	1120
0.12	1.27	45.7	208.8	1.75	5.07	0.1062	1458
0.12	1.27	61.0	371.1	2.59	5.79	0.083	1686
0.12	1.27	76.2	579.8	3.52	6.43	0.0683	1886
0.12	1.27	91.4	835.0	4.53	7.01	0.0581	2065
0.12	0.64	3.81	1.451	0.0302	1.275	0.5591	264.5
0.12	0.64	7.62	5.798	0.1231	2.056	0.2764	540
0.12	0.64	15.2	23.20	0.503	3.319	0.120	947
0.12	0.64	22.9	52.19	0.990	4.418	0.0828	1286
0.12	0.64	30.5	92.97	1.54	4.855	0.0592	1430
0.12	0.64	45.7	208.8	2.79	5.942	0.0404	1769
0.12	0.64	61.0	371.1	4.20	6.829	0.0310	2043
0.12	0.64	76.2	579.8	5.58	7.521	0.0258	2259
0.12	0.64	91.4	835.0	6.96	8.108	0.0223	2435
0.06	1.27	3.81	1.451	0.00381	0.997	≈1	29.89
0.06	1.27	7.62	5.798	0.01476	1.580	0.9998	115.8
0.06	1.27	15.2	23.20	0.0603	2.549	0.9622	455.2
0.06	1.27	22.9	52.19	0.1373	3.372	0.8508	916.4
0.06	1.27	27.4	75.17	0.1989	3.825	0.7746	1209
0.06	1.27	30.5	92.97	0.2463	4.113	0.7257	1402
0.06	1.27	45.7	208.8	0.5609	5.44	0.5283	2325
0.06	1.27	61.0	371.1	0.975	6.57	0.4065	3109
0.06	1.27	76.2	579.8	1.47	7.55	0.3283	3786
0.06	1.27	91.4	835.0	2.00	8.38	0.2773	4351

(1) A_c used in the computation was for 4536 kg (10,000 lbs) carbon or 784.52 m^2 (8444.5 ft^2) of panels.

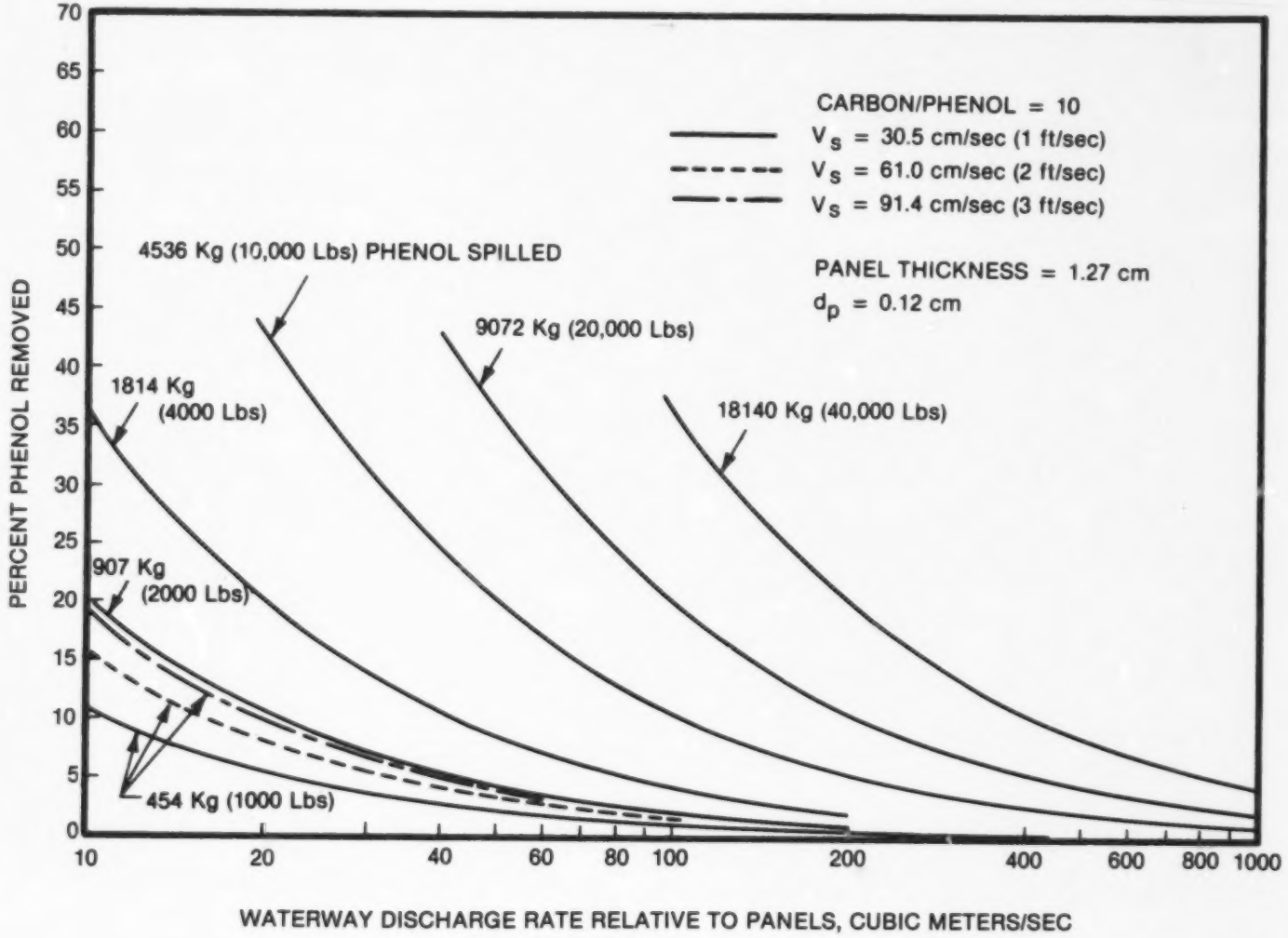


Figure 7. Percent removal of spills from waterways by carbon-filled panels.

velocities of 61.0 and 91.4 cm/sec (2 and 3 ft/sec). It should be noted that increasing v_s from 30.5 to 61 cm/sec (1 to 2 ft/sec) (which also doubles $\overline{Q}$) for a 453.6-kg (1000-lb) spill, for example, will result in a smaller percent phenol removed. For 1.27-cm (0.5-in) -thick panels filled with 0.12-cm carbon granules, the percent removal is maximized at a v_s of about 15.2 cm/sec (0.5 ft/sec). If the river velocity was 61.0 cm/sec (2 ft/sec), for example, and if the panels could be allowed to drift down the river at 45.7 cm/sec (1.5 ft/sec), the calculations indicate the panels would remove more phenol. However, the polluted stretch of water would take four times longer to move past the panels and during this additional time longitudinal dispersion will further dilute the pollutant. The calculations ignore this complicating factor.

Calculations based on Eq. 38 appearing in Table 5 and Figure 7 are good for the first portions of the spill-polluted water to pass through the panel-festooned region of the river. As more of the contaminated water passes through the panel region, Eq. 36 would have to be numerically integrated, taking into account a variation of adsorbed material on the panel, with the axial distance of the panel from the head of the panel region. This is especially true for the large spills and low values of $\overline{Q}$. It is believed that the percent removal results appearing in Figure 7 are higher than can be attained in practice.

Experiments performed by Calspan (Ref. 1) with a 21.3-m (70-ft) -long 0.0929 m^2 (1 ft^2) cross-section recirculation channel containing 1000 liters of water with 250 ppm phenol in which carbon-filled bags, attached to floats, were permitted to drift with the channel current, can be compared with the predictions of Eq. 34. Since the carbon bags drifted with the channel current, the actual value of $\overline{Q}$, the volumetric discharge relative to the bags, is unknown. If the slip velocity is assumed to be 3.81 cm/sec (0.125 ft/sec), $\overline{Q}$ is 1.787 liters/sec (0.0631 ft^3/sec). Using values from Table 5 for v_s = 3.81 cm/sec (0.125 ft/sec), d_p = 0.12 cm, L = 0.64 cm (0.25 in), and a carbon-phenol ratio of 10, Eq. 34 predicts that 7.73% of phenol would be removed per pass of the fluid. One pass requires 560 sec (= 21.3 m/0.0381 m/sec) and 6.43 passes will be made in 1 hour. Hence, Eq. 34 predicts that 100 $(1 - 0.0773)^{6.43}$, or 59.6% of the phenol will remain after 1 hour. This is less than the values obtained by Calspan (Figure 4) for channel currents of 30.5 cm/sec (1 ft/sec) and 15.2 cm/sec (0.5 ft/sec).

TURBULENT DIFFUSION AND DISPERSION IN WATERWAYS

Turbulence and longitudinal dispersion in waterways will serve to dilute spilled water-soluble materials. The dilution can reduce the toxicity of hazardous water-soluble spills to levels that can be tolerated by aquatic life or in drinking water. Dilution, however, also makes it more difficult to remove hazardous water-soluble substances. This section will examine the effect of transverse, or lateral eddy diffusion and longitudinal dispersions on the spread and dilution of a water-soluble spill. The effect of the dilution of the spill on the use of adsorbents will be examined. The treatment given here to the subject of spills cannot be exhaustive. Spill parameters such as the amount of material spilled, the rate and duration of the spill, the size and hydrological properties of the watercourse (velocity, depth, width, slope, discharge and dispersion coefficient) and the spill location (e.g., center of

the river or at the bank) will all affect to some extent the time required for the dilution of the pollutant.

The time-averaged continuity equation for mass transfer in a turbulent field is given by Eq. 20.

$$\frac{\partial \overline{C}}{\partial t} + \overline{v} \cdot \nabla \overline{C} - (\varepsilon_d + \mathcal{D}) \nabla^2 \overline{C} = 0. \tag{20}$$

The eddy diffusivity, ε_d, is a property of the flow field and, unlike $\mathcal{D}$, is independent of the molecular properties of fluid. An expression for the eddy diffusivity in the vertical direction, ε_y, can be obtained for open channel flow from an earlier analysis by substituting Eq. 23 in Eq. 28, i.e.,

$$\varepsilon_y = k u_* y \left(1 - \frac{y}{D}\right). \tag{39}$$

The lateral eddy diffusion coefficient, ε_z, for an open channel flow has been determined experimentally by Elder (Ref. 15) who reported the value

$$\varepsilon_z = 0.23 D u_* . \tag{40}$$

The eddy diffusion coefficients, though quite large in comparison to molecular diffusion coefficients, do not describe the primary dilution action in watercourses, which is longitudinal dispersion. Longitudinal dispersion involves the spreading out of a water-soluble substance (in this case a pollutant spill) along the length of a watercourse due to variations in flow velocity across the channel. An initial analysis of turbulent axial dispersion in pipes by Taylor (Ref. 16) in which it was shown that the process could be described by a one-dimensional form of Eq. 20 (a Fickian diffusion equation),

$$\frac{\partial \overline{C}}{\partial t} + \overline{u} \left(\frac{\partial \overline{C}}{\partial x}\right) = D_x \frac{\partial^2 \overline{C}}{\partial x^2} , \tag{41}$$

where $\overline{C}$ and $\overline{u}$ in Eq. 41 are cross-sectional mean values, and D_x is the longitudinal dispersion coefficient, led to the application of this approach to the study of dispersion in watercourses (Refs. 15 and 17). Methods outlined by Fischer (Ref. 17) permit the evalution of D_x for use in Eq. 41 from field data.

Observed values of D_x for a number of rivers and locations are given in Table 6 (Refs. 18, 19, and 20). The measurements tabulated were obtained using fluorescent dye or radio-isotope tracer techniques. Simplified equations for the calculation of D_x from various river flow parameters are available. Because of the complexity of the river flow processes, these expressions can often be in great error. They are used to estimate D_x when field measurements are unavailable. McQuivey and Keefer (Ref. 18) suggest the equation

$$D_x = 0.058 \frac{Q}{SW} , \tag{42}$$

TABLE 6. SUMMARY OF RIVER FIELD DATA

Watercourse and Test Location	S in 10^{-3}	Q m^3/sec	R cm	W meters	v cm/sec	u_* cm/sec	D_x m^2/sec
Chicago Sanitary & Ship Canal (Calumet Sag)	0.0059	107.1	633	48.8	27.1	1.9	3.56
Missouri River (near Omaha, Nebraska)	0.200	957.1	305	187.8	171	7.7	1490
Clinch River (near Clinchport, Virginia)	0.324	6.80	66.6	34.7	18.1	4.6	19.7
Copper Creek (near Gate City, Virginia)	0.360	9.15	95.3	67.4	18.7	5.8	9.1
Powell River (Sneedville, Tennessee)	0.324	3.96	85.1	34.4	16.4	5.2	26.8
Coachella Canal (Holtville, California)	0.121	37.29	156	24.7	68.3	4.3	17.7
Bayou Anacoco	0.500	13.5	91.4*	36.6	39.6	6.7	39.5
Nooksack River	9.61	32.56	76.2*	64.0	67.1	26.8	34.84
John Day River	1.35	69.09	246.9*	34.1	82.3	18.0	65.0
Sabine River	0.15	389.4	475.5*	127.4	64.0	8.23	669
Green-Duwamish (Seattle, Washington)	0.224	8.78	110	29.9	32.0	4.9	6.5

* Mean depth.

where S is the slope of the channel bed and W is the channel width, while Fischer (Ref. 19) proposed the formula

$$D_x = \frac{0.011\ vW}{D_1\ u_*} . \tag{43}$$

A more recent (1978) analysis of dispersion in natural streams by Liu (Refs. 20 and 21) has resulted in the equation

$$D_x = 0.5\ \frac{u_*\ Q^2}{V^2\ R^3} , \tag{44}$$

where R is the hydraulic radius.

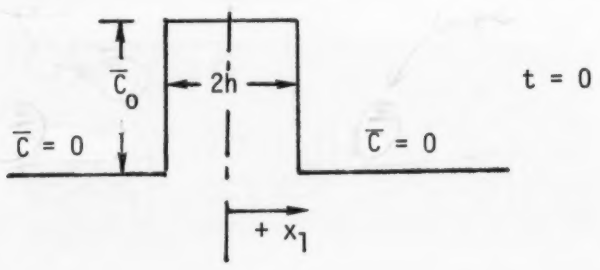
Making the substitution $x_1 = x - \bar{u}t$ in Eq. 41 reduces it to

$$\frac{\partial \bar{C}}{\partial t} = D_x \frac{\partial^2 \bar{C}}{\partial x_1^2} . \tag{45}$$

Solutions to Eq. 45 for various boundary conditions are given by Crank (Ref. 23). For dispersion of an amount of substance M deposited at t = 0 in the plane $x_1 = 0$, Crank gives

$$\bar{C} = \frac{M}{2(\pi D_x t)^{1/2}} \exp\left(-\frac{x_1^2}{4D_x t}\right) . \tag{46}$$

It should be remembered that $\bar{C}$ in Eqs. 45 and 46 is the mean concentration taken over a cross-sectional area of the watercourse at x_1 and that $\bar{M}$ should be in units of mass (or moles) per unit cross-sectional area. Equation 46 can be used to determine curves of $\bar{C}$ vs x_1 for various times for "instantaneous" spills. For more flexibility in specifying the rate of spill, solutions can be obtained for a solute of concentration $\bar{C}_o$ initially confined in the region $-h < x < h$ as shown below



The solution given by Crank (Ref. 23) is

$$\frac{\bar{C}}{\bar{C}_o} = \frac{1}{2}\left(\text{erf}\,\frac{h-x_1}{2\sqrt{D_x t}} + \text{erf}\,\frac{h+x_1}{2\sqrt{D_x t}}\right). \quad (47)$$

Knowing the mean river velocity, the spill rate, and the volumetric flowrate of the river, one could calculate $\bar{C}_o$ and h.

Equation 47 was used to determine mean concentration vs distance profiles for phenol spills of 18,144 kg (40,000 lbs) or 16.96 m^3 (599.09 ft^3) and of 1814 kg (4000 lbs) or 1.696 m^3 (59.9 ft^3) at a spill rate of 3.54 m^3/min (125 ft^3/min) into the Chicago Sanitary & Ship Canal (CSSC). Using data given in Table 6 for v, Q, the half width h for the 18,144-kg (40,000-lb) spill is 39.0 meters and $\bar{C}_o$ is 549.5 ppm by volume; for 1814 kg (4000 lbs), h = 3.90 meters and $\bar{C}_o$ is 549.5 ppm by volume. Using these values and D_x for the CSSC, Eq. 47 was used to compute $\bar{C}$ vs x_1 profiles plotted in Figure 8 for t = 1, 2, 4, and 8 hours. According to Fischer (Ref. 17), the duration of an initial period in which the longitudinal dispersion is not properly described by the one-dimensional mass diffusion equation, Eq. 41, is greater than 6 times the Lagrangian time scale. The time is given by the equation

$$t' > 1.8\,\frac{\ell^2}{Ru_*}. \quad (48)$$

Using Eq. 48 and data on the CSSC, t' is determined to be greater than 2.48 hours. Thus, the curves appearing in Figure 8 are probably valid representations of the concentration-distance profile.

The CSSC was chosen for the dispersion calculation because it was undoubtedly used for shipping and had the smallest dispersion coefficient in Table 6. It is believed that the concentration profiles in Figure 8 provide conservative values of the spill dilution that would occur in rivers of comparable flowrate.

Calculations have been made of the concentration-lateral distance profiles as a function of time resulting from lateral eddy diffusion processes. Longitudinal spreading of the pollutant was ignored. The solution to the one-dimensional diffusion equation written for the z direction was obtained from Crank (Ref. 23) for the diffusion of a substance initially confined in the region $-h < x < h$, into a field of width W (i.e., at $z \pm W/2$, $\partial C / \partial z = 0$), i.e.,

$$\frac{C}{C_o} = \frac{1}{2}\sum_{n=-\infty}^{\infty}\left\{\text{erf}\,\frac{h + nw - z}{2\sqrt{\varepsilon_z t}} + \text{erf}\,\frac{h - nw + z}{2\sqrt{\varepsilon_z t}}\right\}. \quad (49)$$

A uniform flow, v, can be imposed on the solution, Eq. 49, by merely associating the profile calculated for time t with a distance vt downstream from the spill point.

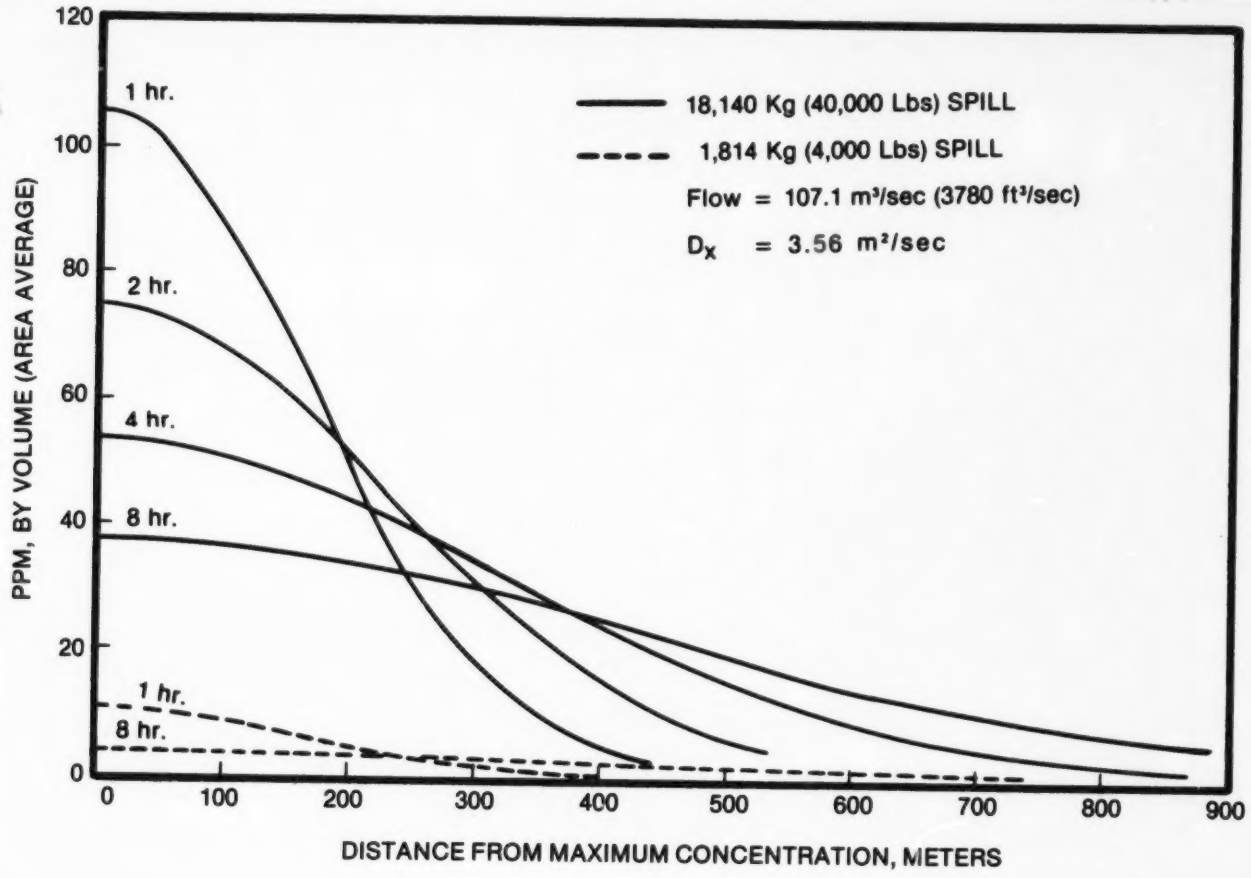
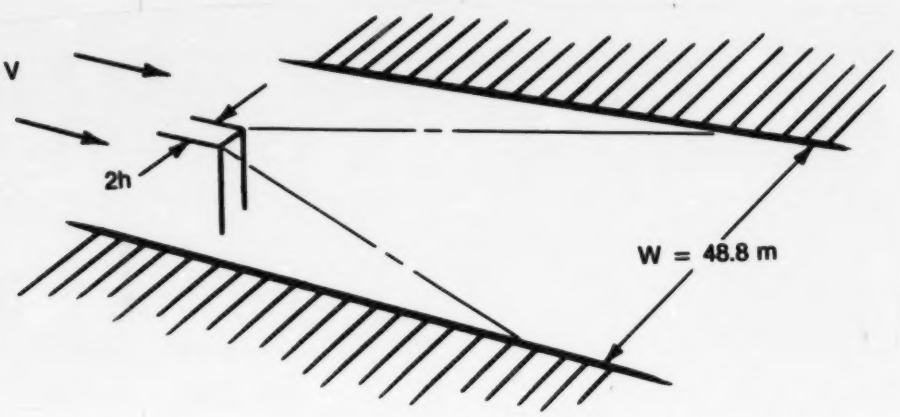


Figure 8. Longitudinal dispersion of water-soluble spills in the Chicago Sanitary and Ship Canal

The spill may be viewed as a slot source of area 2hD, through which pollutant enters the watercourse at velocity v as shown below:



For a spill rate of 3.54 m^3/min (125 ft^3/min) of phenol into the CSSC, 2h was computed to be 2.69 cm. The calculated transverse profiles are given in Figure 9.

A lateral eddy diffusion coefficient of 276.6 cm^2/sec was calculated using Eq. 40 and data from Table 6. The concentration profiles computed from Eq. 49 and given in Figure 9 show how quickly eddy diffusion will spread a spilled water-soluble substance across the watercourse. In only 3 hours the concentration at the bank of the river is 97.4% of the concentration at the center. Profiles given in Figure 9 were for a spill at the center of the watercourse. Concentration profiles can be computed for spills at any point from the center of the channel to the bank by using the method of reflection and superposition (Refs. 22 and 23). Indeed, Eq. 49 is merely a special case for a centrally located source. Had the spill occurred at the bank rather than at the center of the channel (the worst case with regard to time), computations reveal that in 10 hours the concentration at the opposite bank of the river would be 93.6% of that on the bank where the spill occurred. Equation 49 can be utilized to compute the bank spill profiles by doubling the value of h and W and solving for one-half of the profile (the curves in Figure 9 represent profiles for 1.77 m^3/min (62.5 ft^3/min) spills at the bank of a 24.4-m-wide river as well as 3.54 m^3/min (125 ft^3/min) spills at the center of a 48.8-m-wide river.

The lateral location of the spill is usually of minor importance unless the width of the river is quite large; the time required for turbulent eddy diffusion to spread a water-soluble chemical across the river is probably less than would be required to notify emergency response teams and marshal resources for attempts at cleaning up the spill.

HAZARDOUS MATERIAL SPILL STATISTICS

A recent compilation and analysis of hazardous material spills based on approximately 1500 reported incidents from January 1971 to June 1973 (Ref. 24)

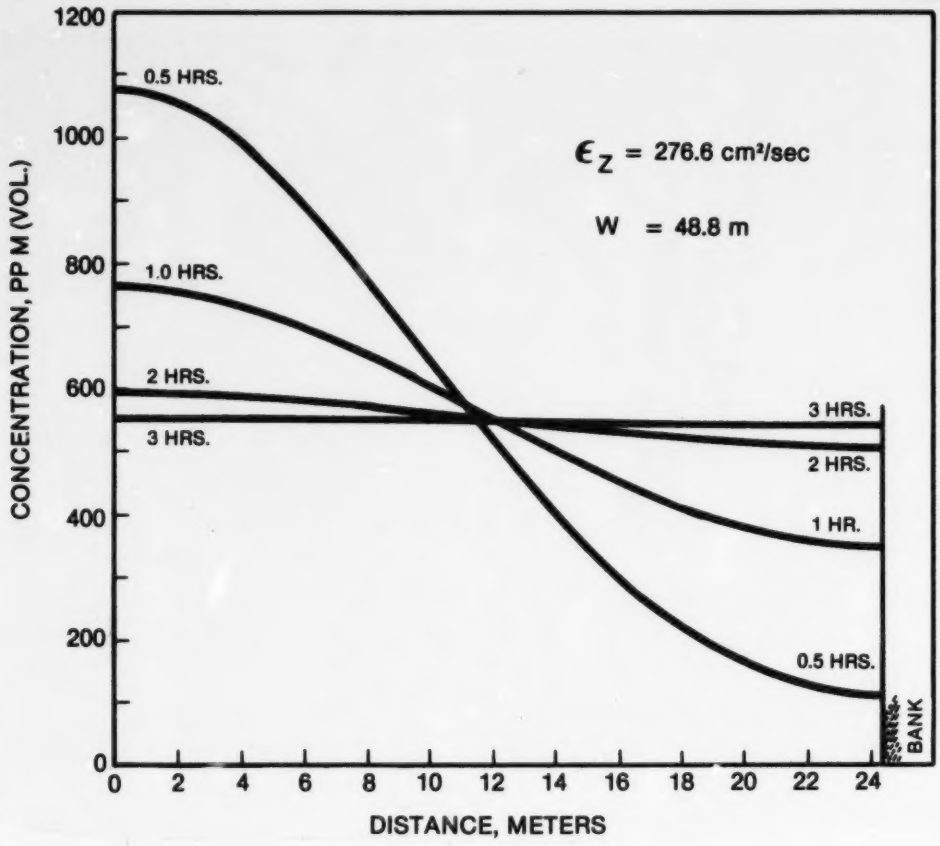


Figure 9. Transverse concentration profiles - water-soluble spill at center of Chicago Sanitary and Ship Canal.

and information and studies published by others (Ref. 25) have provided some useful statistics. Information on the weight percent of hazardous materials shipped by various means, the percentage spilled during transport and from stationary sources, and the percent reaching surface water are given in Table 7. Unfortunately, there is no information on the size distribution of the receiving waters exposed to these spills.

With regard to phenol, the hazardous material of interest to this study, data on the reported spill size and number of occurrences are given in Table 8 (Refs. 24 and 25). About 293,000 liters of phenol were spilled in 19 reported incidents; in six other reported cases the amount of phenol was not given. The three largest phenol spills (Table 8) were all the result of train derailments and appear to be in a class by themselves. Together, they account for 85.3% of the total volume of phenol spilled in the 2.5-year time interval. Twelve of the remaining 16 incidents listed with a spill volume in Table 8 involve less than 453.6 kg (1000 lbs) each and the other four range from about 4040 to 20,320 kg (8900 to 44,800 lbs) of phenol. These data are in keeping with the general conclusions of the spill study (Ref. 24) that spills resulting

TABLE 7. HAZARDOUS SPILL STATISTICS (Refs. 24 and 25)

	% Wt of all Shipments	% Shipment Spilled	Total Transp. Spillage	% Total Spillage	% Spillage Reaching Water	% Total Spill Entering Water
Rail	13.3	0.0536	45	26	15	4
Barge	32.1	0.0111	22	12	68	8
Truck	54.6	0.0095	33	19	42	8
Stationary Source	--	--	--	43	59	25
Total	100%		100%	100%		45%

TABLE 8. PROFILE OF PHENOL SPILLS (Refs. 24 and 25)

Average Spill Size (liters)	(kilograms)	Percent of Total Spill Volume Represented*	Number of Events
Unknown	--	--	6
0 - 50	0 - 53.5	0.10	8
50 - 385	53.5 - 411	0.37	3
385-3,800	411 - 4,055	1.30	2
8,000	8,528	2.73	1
11,000	11,750	3.75	1
19,000	20,280	6.48	1
80,000	85,300	27.29	1
83,000	88,450	28.31	1
87,000	93,000	29.68	1

* Total spillage reported = 293,000 liters from 1971-1973.

from tank ruptures and punctures have by far the greatest probability of high hazard potential. The fourth largest spill in Table 8, a 20,320-kg (44,800-lb) spill from a railroad tank car puncture, if added to the train derailment total, would bring the tank failure total to 91.8% of the total spillage.

Dividing the phenol spills into rail, truck, barge, and stationary source categories and multiplying each by a probability obtained for all hazardous materials (Table 7), one would surmise that about 20,240 liters, or 21,600 kg (47,600 lbs) of phenol entered surface waters in the average year from 1971 to 1973. If, as stated in Ref. 25, 15% of spill volume from rail accidents enter surface waters, a rail tank car failure would send an average of about 12,700 to 14,600 kg (28,000 to 32,200 lbs) of phenol into rivers or lakes. Of course, averages and probabilities are given, not certainties. It could well be that one accident would result in 45,400 to 90,700 kg (100,000 to 200,000 lbs) entering a watercourse, while several other tank car spills would not reach a waterway. It seems very unlikely, however, that the entire contents of a tank car spill would enter a waterway unless the derailment or other rail accident took place on a bridge.

Curiously, none of the phenol spills listed were the result of a barge accident, although 32.1 weight percent of all hazardous material shipments are reportedly transported by barge.

SECTION 5

DISCUSSION

A model for the use of containers of carbon adsorbent to remove water-soluble pollutants spilled into waters has been presented and analyzed. Figures and tables have served to summarize the computed performance of the model systems. For simplicity, the computed performance was given without consideration for the coupling of turbulent mixing and dispersion in waterways. This coupling is further complicated by (a) the dependence of the spill dilution rate on the relationship between the size of the spill and the volumetric flowrate of the affected waterways, and (b) the reaction time of an emergency response team. To correspond to the real world, consideration must also be given to spill statistical data. What size spills of a given hazardous material will occur with what frequency or probability, into what size waterways? These areas have all been addressed more or less separately in the previous analysis section.

With regard to the interaction between dilution by turbulent mixing and dispersion, and the adsorption process, these processes could have been described in a single equation of the form

$$\frac{\partial C}{\partial t} = D_x \frac{\partial^2 C}{\partial x^2} - KC\frac{N}{V} , \qquad (50)$$

where KCN/V is the rate of change of concentration with respect to time due to adsorption. The term K can be defined by reference to Eqs. 11 and 12, depending on the buoyant packet model being applied. The coupling of the longitudinal dispersion equation and the adsorption equation for panels is somewhat more complicated because the adsorbing panels are in a fixed location in the flowing stream and not uniformly distributed throughout the diffusing volume as is assumed in Eq. 50.

Spill statistics for phenol gathered from 1971 to 1973 (Refs. 24 and 25) indicate that it is unlikely that a single spill will result in more than 18,140 kg (40,000 lbs) of phenol entering a waterway. In the examples to be used, 1814- to 18,140-kg (4000- to 40,000-lb) phenol spills will be the maximum considered. Since no barge incidents appear in the statistics, the maximum number may be somewhat optimistic.

The waterway used in the examples as a typical navigable waterway for commerce is the Chicago Sanitary and Ship Canal (CSSC). While its flowrate of 107.1 m^3/sec (3780 ft^3/sec) may be average, the measured dispersion coefficient, D_x, was the lowest value found; this is probably because it is a straight,

relatively smooth, man-made canal. For a comparable natural watercourse, D_x would be 10 times that of the CSSC. The amount of dilution occurring in the CSSC is probably representative of a natural watercourse with a flowrate of about one-third that of the CSSC, or about 35.4 m^3/sec (1250 ft^3/sec).

A large, non-impoundable waterway, one in which the polluted stretch of the waterway could not be confined behind a holding dam or diverted to some holding area for treatment by other than in-situ methods, will be taken arbitrarily here to be a waterway with a flowrate exceeding 850 m^3/sec (30,000 ft^3/sec).

EFFECTIVENESS OF BUOYANT PACKETS

The equations derived for the adsorption rate of pollutant from waterways by in-situ application of buoyant carbon-filled packets (Eqs. 11 and 13) contain the total volume of fluid to be treated, V, in the denominator. As a result, an increase in V with time resulting from turbulent mixing and dispersion in waterways will increase either the number of cycles or the suspension time required to remove a specified fraction of the pollutant, unless the number of carbon packets is also increased with time so as to maintain N/V constant.

As indicated elsewhere in this study, it does not appear possible to maintain buoyant packets in suspension with any degree of uniformity by the turbulence of a waterway. The distribution given in Figure 5 requires that the packet concentration be measured at some point between $y' = 0.05D$ and $y' = D$; it does not yield information on the packet population that merely floats on the surface. It is believed that very few packets will be below the water surface. However, the turbulence of a watercourse and the swirling action induced by the pumped fluid and packets injected near the channel bottom might cause the actual suspension time of the packets to be longer than D/v_t. Perhaps Eq. 10 could be rewritten with D/v_t multiplied by some correction factor to be determined experimentally.

Responding to an 1814-kg (4000-lb) phenol spill into the CSSC with 18,140 kg (40,000 lbs) of activated granular carbon and 8645 kg (19,060 lbs) of flotation material in 897,000 buoyant packets within 1 to 8 hours would mean removing phenol from a mixture in which the maximum concentration would be between about 4 ppm and 14.5 ppm (10.5 ppm cross-sectional area mean) by volume (from Figures 8 and 9) dissolved in roughly 3×10^5 to 6.8×10^5 m^3 (80×10^6 to 180×10^6 gal) of water (ignoring the portions of the canal where the calculated phenol concentration is less than 0.5 ppm) spanning a distance of 800 to 1800 meters along the channel. For a response 1 hour after the spill, calculations (Eq. 11) indicate that a 10% reduction in phenol concentration would require 155 cycles of the packets; after 8 hours, 368 cycles would be needed to effect a 10% reduction in concentration. Using a factor of 15% solids by volume that can be handled by the pumps, this would mean that 6.07×10^4 m^3 (16.05×10^6 gal) to 1.44×10^5 m^3 (38.1×10^6 gal) of water and packets must be pumped (391.8 m^3/cycle [103,500 gal/cycle]). If it were possible to reduce the packet cycle time to 10 minutes, the time required for 155 cycles (starting cleanup operations 1 hour after the spill) would be 25.8 hours, while 368 cycles (starting 8 hours after the spill) would take 61.3 hours. The solids-handling

pumps would have to circulate 39.4 m^3/min (10,400 gal/min). Of course, during the cleanup process the phenol will continue to spread longitudinally along the channel.

If it were possible to keep the buoyant packets suspended in the CSSC by turbulence (which appears to be highly unlikely), a response to the 1814-kg (4000-lb) spill in 1 to 8 hours would produce a situation in which from 25 to 60 hours would be required to remove 10% of the spilled phenol, even if the dispersion process were to cease.

For an 18,140-kg (40,000-lb) spill of phenol into the CSSC, a response within 4 hours with 181,400 kg (400,000 lbs) of carbon and 86,450 kg (190,600 lbs) of flotation material contained in 8,973,620 packets would have to deal with about 6.32×10^5 m^3 (167×10^6 gal) of water containing an average of about 27 ppm phenol (by volume). Using Eq. 11, we find that 32.35 cycles of the packet population are needed. This would require the pumping of 1.27×10^5 m^3 (33.5×10^6 gal) of water and packets. The time needed for one cycle will depend either on how rapidly 8.974×10^6 packets can be retrieved and prepared for reinjection by pumping, or on the available pumping capacity.

An optimistic cycle time of 10 minutes would result in a total time of 5.4 hours to remove 10% of the spill and a pumping rate of 394 m^3/min (104,000 gal/min). During the 5.4 hours, even without cleanup, dispersion processes would reduce the average concentration of phenol to about 19 to 20 ppm and increase V by 30% to 40% (as stated previously, the interaction of dispersion and adsorption could be more accurately described by solutions to Eq. 50). The effect of on-going dispersion would be to increase the number of cycles required to remove 10% of the pollutant.

It should be noted that Eq. 11 relates the natural log of the concentration change to Nn. Attempts to remove pollutant faster by increasing N will only decrease n in direct proportion. There will be fewer cycles but more packets to retrieve and pump in each cycle; the volume of material pumped into the channel (NnV/0.15) will not change.

CARBON-FILLED PANELS

Unlike the equations derived for the buoyant packets, the volume of water to be treated does not appear in Eq. 38, the equation derived for the adsorption by panels hanging in a waterway. The fraction of pollutant removed is directly proportional to the panel area facing the flow and inversely proportional to the volumetric discharge rate relative to the panels.

Carbon panels fixed in a watercourse of the size of the CSSC will remove about 4% of an 1814-kg (4000-lb) phenol spill as the polluted fluid passes by the panels according to the model used to compute Figure 7. Since the percent of spill adsorbed is directly proportional to the total panel area, facing the flow, if the carbon-to-phenol ratio was 100, that is, if 181,400 kg (400,000 lbs) of carbon were used to clean up a 1814-kg (4000-lb) spill, then theoretically as much as 33% of the phenol could be removed. The computation was made assuming v_s = 22.86 cm/sec (0.75 ft/sec) and using data in Table 5 with Eq. 38.

It has been assumed in this work that equilibrium is rapidly established at the activated carbon surface, i.e., the concentration at the fluid-exterior particle interface is that value dictated by the adsorption isotherm. When working with fluids containing 100 ppm of dissolved pollutant, the neglect of small deviations from equilibrium at the fluid-particle interface (say 1 or 2 ppm) will cause errors of a few percent in the computations. However, when the fluid contains an average of less than 5 ppm of pollutants, as it does after 8 hours of dispersion of a 1814-kg (4000-lb) spill into the CSSC, the neglect of similar deviations from equilibrium can result in substantial errors in the computations.

In the event of a massive spill such as 18,140 kg (40,000 lbs) of phenol into the CSSC, the computations indicate that the use of 181,400 kg (400,000 lbs) of carbon in 1.27-cm (0.5-in) -thick panels could remove as much as 33% of the phenol. The relative size of the spill with regard to the volumetric flowrate of the channel and the dispersion coefficient, results in an average concentration of about 20 ppm over 2000 m of the canal and about 12 ppm after 24 hours. An 18,140-kg (40,000-lb) spill into a larger, non-impoundable river such as the Missouri River (Table 6) would be rapidly diluted, i.e., after 1 hour the maximum concentration (cross-sectional area average) calculated using Eq. 47 would be about 3.44 ppm. Using Eq. 48, the estimated time required after the spill for the Fickian equation (Eq. 45) to become strictly applicable is estimated to be 18.6 hours. After that length of time, the maximum area average concentration of phenol in the channel was calculated to be 0.707 ppm. According to Eq. 38, about 4.7% of the phenol could be recovered. The low phenol concentrations found in the river after a few hours would indicate that 4.7% is highly optimistic. The calculated percent removal will be in error on the high side if the concentration of phenol at the fluid-carbon external surface deviates from the equilibrium value obtained from an adsorption isotherm. If the concentration at the external interface of fresh carbon was 1 ppm, for example, and the bulk concentration was 2 ppm, the percent recovery would be reduced by a factor of 2.

During the course of this study a number of assumptions and idealizations have been made. Whenever possible, they have been made so as to present an optimum situation for the carbon packets and panels, i.e., the results given here are believed to be more favorable than can be realized in practice. The reasons for this are:

a. The assumption that packets and panels are always turned broadside to the flow

b. The neglect of flow resistance offered by the fabric that would be used to encase the adsorbent

c. The assumption of negligible resistance to mass transfer in the solid-phase and the assumption of equilibrium concentration at the external fluid-solid interface

d. The assumption that fluid leaving a packet or panel is well mixed with the surrounding fluid in the waterway before entering another packet or panel

e. The assumption that adsorbent particles in the packets and panels will remain distributed in a uniform bed thickness over the entire flow cross-section

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APPENDIX A

PROPERTIES OF ACTIVATED CARBON AND PACKETS

The calculations performed for this study used the following values of physical properties for carbon:

Real density	2.14 gm/cc
Bulk density	0.456 gm/cc
Particle density	0.747 gm/cc
Wet particle density	1.35 gm/cc
Volume fraction of pores	0.651
Void fraction in beds	0.39

Figure A-1 is the phenol-carbon (Nuchar C-190) isotherm used in this study (Ref. 2).

The flotation particles required to buoy packets of carbon were assumed to have a density of 0.20 gm/cc and the same d_p as the carbon

The packet density ρ_p is given as

$$\rho_p = 0.61\ [0.2\psi + 1.35\ (1-\psi)] + 0.39. \qquad \text{(A-1)}$$

The mass of carbon, m_c, in a packet of volume V_p is

$$m_c = 0.61 \cdot 0.747\ (1-\psi) V_p\ . \qquad \text{(A-2)}$$

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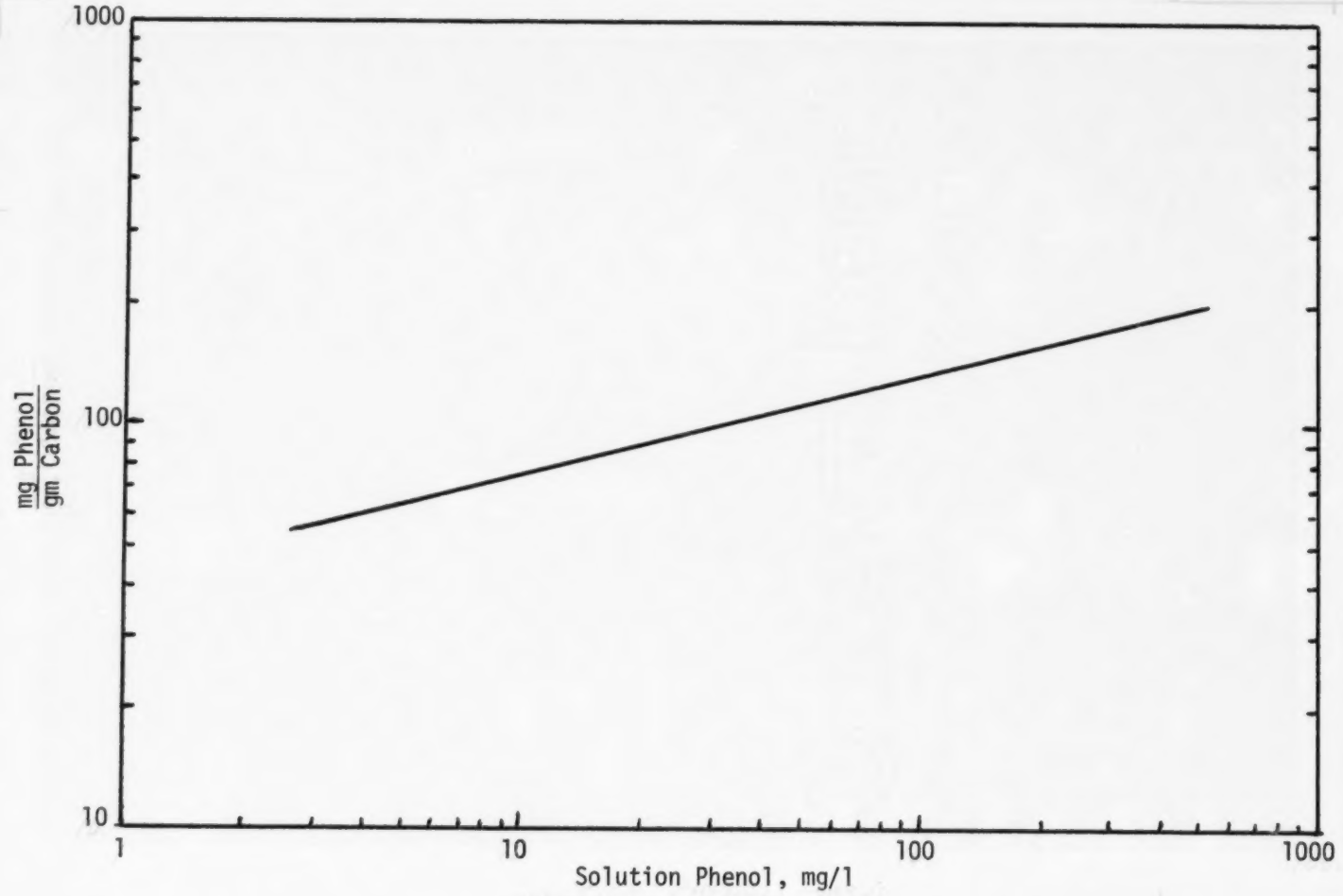

Figure A-1. Adsorption isotherm for phenol and activated carbon - Nuchar C-190 (Ref. 2).

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APPENDIX B

APPLICATION OF ION-EXCHANGE RESINS TO HAZARDOUS SPILLS IN WATER

The mass transfer model used in this study of the application of thin packets and panels filled with activated carbon to the removal of dissolved hazardous materials from water can be easily extended to ion-exchange resins. Most of the procedures and equations outlined for activated carbon can be applied to the analysis of packets and panels filled with ion-exchange particles. The one exception may be the inclusion of a solid-phase mass transfer term for ion-exchange particles. In the activated carbon packet study, the mass transfer resistance due to processes occurring inside the particle (diffusion through the pores and along the solid surface inside the particle, and the physical adsorption at active sites) were assumed to be negligible in comparison with the fluid-side resistance. For ion-exchange resins this assumption may not be valid. Inclusion of an added resistive step, regardless of how small, must reduce the overall mass transfer rate. The adsorption rates computed for carbon in this report are, in this respect, optimistic.

For ion-exchange particles, the computation and addition of a term for solid-phase resistance can be accomplished. The reader is referred to the detailed explanation, discussion, and examples given in Sherwood, Pigford, and Wilke (Ref. 14) which will be followed here.

The procedure of Thomas as given in Ref. 14, in which the rate of adsorption is described in a form similar to a "kinetic driving force" suggested by the stoichiometry of a monovalent ion-exchange reaction, i.e.,

$$Na^+ + RH \rightarrow H^+ + RNa$$

$$c\,,\ q_m - c \qquad C_o - C\,,\ q\,.$$

At equilibrium,

$$K = \frac{[H^+]\,[RNa]}{[Na^+]\,[RH]}\,.$$

The rate expression for the packet then becomes

$$\rho_b \frac{\partial q}{\partial t} = k_o a \left[C \left(1 - \frac{q}{q_m} \right) - \frac{q}{K q_m} (C_o - C) \right]. \qquad \text{(B-1)}$$

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Since the mass adsorbed must pass through the fluid film surrounding the particle and through the resistance inside the particles, Eq. B-1 can be equated to expressions as

$$k_o \left[C \left(1 - \frac{q}{q_m} \right) - \frac{q}{Kq_m} (C_o - C) \right] = k_c (C - C_i) = \frac{k_s}{\rho_b} (q_i - q), \quad \text{(B-2)}$$

where

$$q_i = q_m \frac{K C_i}{C_o + (K-1) C_i} . \quad \text{(B-3)}$$

For the special condition $C = C_o/2$, Eq. B-2 can be reduced to a form that can be solved simultaneously with Eq. B-3 to find C_i, given K, C_o, and $q_m k_s/\rho_b C_o k_c$ (Ref. 14). The result can be used to find either k_o/k_c or $k_o/(k_s/q_m/\rho_b C_o)$.

The resulting relationship for k_o is obtained (Ref. 14)

$$\frac{1}{k_o} = \frac{1}{B} \left(\frac{1}{k_c} + \frac{C_o}{\rho_b q_m k_s} \right), \quad \text{(B-4)}$$

where the B factor is given in Figure 10.15 of Sherwood, Pigford, and Wilke (Ref. 14).

The value of k_s, the mass transfer coefficient for solid phase, can be obtained using the equation

$$k_s = \frac{10 \mathscr{D}_s}{d_p (1-\theta)} \quad \text{(B-5)}$$

recommended by Vermuelin, Klein, and Hiester (Ref. B-1). $\mathscr{D}_s$ is the diffusion coefficient inside the particle (e.g., Ref. B-2).

Inside a packet of adsorbent

$$\rho_b \frac{\partial q}{\partial t} = - \overline{U}_a \frac{\partial C}{\partial x} . \quad \text{(B-6)}$$

Using Eq. B-4 to find a value for k_o and combining Eq. B-6 with Eq. B-1, an equation is obtained that can be solved numerically for the concentration change across a packet or panel, $(C - C_{out})$. The amount of pollutant removed from a volume, V, of water by N buoyant packets rising through a depth D at v_t can be determined and the total amount for a cycle is

$$V\Delta C = \frac{D}{v_t} \overline{U}_a A_p N (C - C_{out}) + V_p \theta (C - C_i) N . \quad \text{(B-7)}$$

For suspended packets Eq. 14 would be modified to yield

$$- V\frac{dC}{dt} = \overline{U}_a A_p N \, (C-C_{out}) \qquad \text{(B-8)}$$

and Eq. 36 for panels festooned in a homogeneous pattern in a watercourse, will become

$$- v_s \frac{\partial C}{\partial x} = \overline{U}_a a_x \, (C-C_{out}) \qquad \text{(B-9)}$$

or

$$- \frac{dC}{(C-C_{out})} = \frac{\overline{U}_a}{\overline{Q}} \, dA_c \, , \qquad \text{(B-10)}$$

where dA_c is the panel cross-sectional area for flow, distributed in distance dx down the watercourse. Since generally C_{out} will not be found in closed form as a simple function of the concentration entering the packet or panel, Eqs. B-7, B-8, and B-10 will have to be solved numerically along with Eq. B-1.

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APPENDIX C

FREE DISPERSED CARBON PARTICLES

The action of loose, or free carbon particles in a polluted well-stirred volume can be described by the expression

$$- V\frac{dC}{dt} = k_c \pi d_p^{\,2} \overline{N}(C - C_i), \qquad \text{(C-1)}$$

where $\overline{N}$ is the number of carbon particles of diameter d_p suspended in volume V. Letting $\overline{N}\pi d_p^2/V = a$, where a is the external area of the particles per unit volume,

$$- \frac{dC}{dt} = k_c a\,(C - C_i). \qquad \text{(C-2)}$$

Separating variables and integrating, we find

$$\ln\left(\frac{C-C_i}{C_o-C_i}\right) = - k_c a t\,. \qquad \text{(C-3)}$$

For small values of t (when carbon is fresh)

$$\ln\frac{C}{C_o} = - k_c a t. \qquad \text{(C-4)}$$

From experiments conducted by Calspan (Ref. 1) for loose carbon granules in a stirred beaker containing 250 ppm phenol, the slope d ln C/dt at small t was measured to be 0.74 hr^{-1}. Assuming d_p = 0.12 cm and using a carbon-phenol ratio of 10 with ρ = 0.747, a is found to be 0.167 cm^{-1}. For this value of a, $k_c = 1.23 \times 10^{-3}$ cm/sec.

Experiments with fibrous carbon under similar conditions (Ref. 1) yields d ln C/dt = 2.81. Whether k_c is higher for fibrous carbon depends on the value of a for this material. Using $\rho \simeq 1$ given for the fibrous carbon (Ref. 1), it can be shown that $a = 0.01/d_j$ for a carbon-phenol ratio of 10, where d_j is the diameter (cm) of the carbon fiber. The value of k_c for fibrous carbon is then $0.0781\, d_j$ cm/sec. If d_j = 0.0158 cm (for the fibrous carbon used in Calspan's experiment), the mass transfer coefficients for granular and fibrous would be identical. Since the slip velocity of fluid flowing past the carbon fibers is bound to be greater than v_s for small particles being stirred in a beaker, it is expected that the liquid side mass transfer coefficient for the fiber is higher than for the particles.

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Estimates of the mass transfer coefficients for suspended single particles can be obtained by using the procedure recommended by Harriott (Ref. C-1) in which the slip velocity is taken to be the terminal velocity of the particle falling or rising through quiescent fluid under the influence of gravity. This velocity is then used to obtain k_c via a Frössling-type equation, i.e.,

$$\frac{k_c d_p}{\mathcal{D}} = 2 + 0.6\ Re^{1/2}\ Sc^{1/3} . \qquad (C\text{-}5)$$

Using Harriott's approach, the values of k_c given in Table C-1 were determined for carbon particles.

TABLE C-1. CALCULATED MASS TRANSFER COEFFICIENTS FOR FREE DISPERSED CARBON PARTICLES

		Harriot's Approach		Brian & Hales' Correlation	
d_p (cm)	a^* (cm^{-1})	$k_c \times 10^3$ (cm/sec)	$k_c a^*$ (hr^{-1})	$k_c \times 10^3$ (cm/sec)	$k_c a^*$ (hr^{-1})
0.12	0.0669	4.25	1.02	1.06	0.256
0.06	0.134	4.31	2.08	1.29	0.621
0.01	0.803	4.05	11.7	3.18	9.19

*Assuming 100 ppm contaminant and 10/1 ratio of carbon to contaminant.

Very similar values of k_c will be obtained by using the Ranz and Marshall correlation (Ref. C-2) for mass transfer to spheres in a fluid stream if Re is calculated using the terminal velocity of the carbon particle as the slip velocity. This correlation is also plotted in Figure 6.9 of Sherwood, et al. (Ref. C-3).

It may also be possible to determine k_c for particles in rivers by relating k_c to the rate of energy dissipation per unit mass (E) for rivers, that is, applying the theory of local isotropic turbulence of Kolmogarov. One would then utilize a correlation such as that developed by Brian, Hales, and Sherwood (Ref. C-4), given as Figure 6.11 in Sherwood, Pigford, and Wilke (Ref. C-3). The rate of energy dissipation per unit mass for a river flowing at a constant velocity v down a slope S is

$$E = vgS, \qquad (C\text{-}6)$$

where g is the acceleration due to gravity. One would assume here that the turbulence is sufficient to keep the particles suspended in the fluid.

For the Chicago Sanitary & Ship Canal, v = 27.1 cm/sec and $S = 5.9 \times 10^{-6}$, thus E = 0.1567 ergs/gm-sec. Using the Brian and Hales correlation (Ref. C-4),

the values given in Table C-1 for various particle sizes were calculated. The correlation of Levin (Ref. C-5),

$$\frac{k_c d_p}{\mathscr{D}} = 2 + 0.47 \left(\frac{d_p^{4/3} E^{1/3})}{\nu} \right)^{0.62} Sc^{0.36}, \qquad (C\text{-}7)$$

yields quite similar values of k_c.

Comparing values of $k_c a$ for dispersed particles given in Table C-1 with ξ given for packets in Table 3 of this feasibility study, it is seen that for d_p values of 0.12 and 0.06 cm, the values of $k_c a$ and ξ are fairly close.

It appears that free dispersed particles of 0.06 and 0.12 cm diameter will have overall coefficients that are in the same ballpark as the packets attain at the higher buoyancy forces. The main advantage of powdered carbon (0.01 cm) is apparently the increase in the value of a, the external particle area per unit volume of fluid. The Harriott approach yields a value of k_c which is very nearly independent of d_p.

The value of 1.23×10^{-3} cm/sec determined from Calspan's experiment with loose particles of 8 x 30 mesh is fairly close to the values of k_c obtained in this study from literature correlations of fluid-side mass transfer.

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